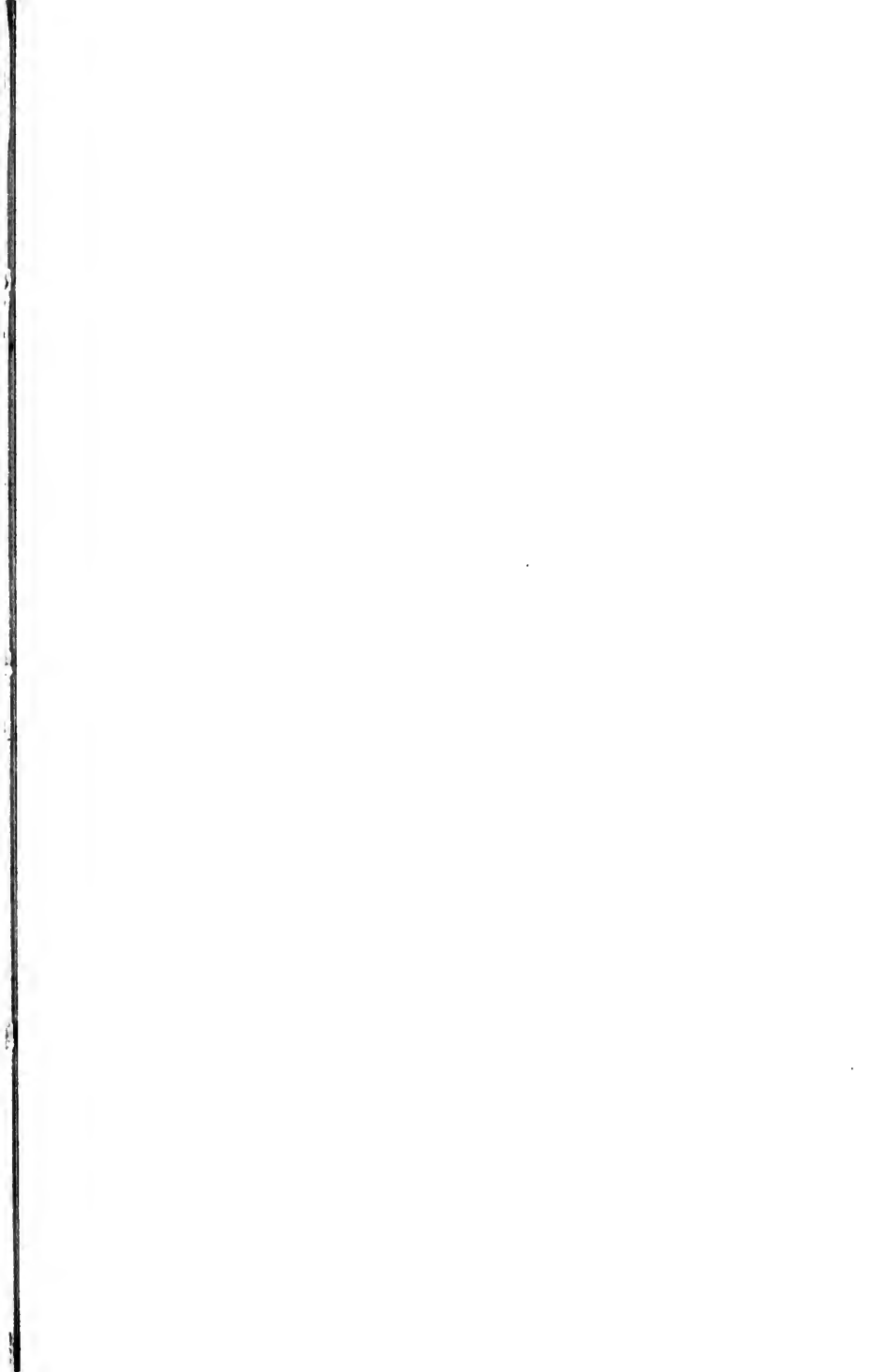


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### ORGANIC CHEMISTRY.

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# JOURNAL

OF

## THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

### PART I.

#### Organic Chemistry.

**Purification of Acetylene.** By FRITZ ULLMANN and IRMA GOLDBERG (*Chem. Centr.*, 1899, ii, 19—20; from *J. Gasbel.*, 42, 374—377).—The phosphorus and sulphur in samples of acetylene which had been purified by various methods were estimated by Lunge and Cedercreutz's method (*Abstr.*, 1898, ii, 54). The results showed that ferric and chromic salts have no purifying effect on crude acetylene, and that whilst cuprous chloride removes hydrogen phosphide but not organic sulphur compounds, chromic acid absorbs, not only the phosphorus compounds, but also almost all those containing sulphur.

The chromic acid contained in the solution used for purifying acetylene is estimated as follows. 25 grams are boiled with 100 c.c. of a 5 per cent. sodium hydroxide solution, the cooled liquid made up to a litre, and 50 c.c. then treated with 8 c.c. of a 10 per cent. solution of potassium iodide, together with about 18 c.c. of a 20 per cent. solution of hydrochloric acid, 200 c.c. of water, and a slight excess of sodium thiosulphate solution. The excess of thiosulphate is titrated with iodine solution. The results obtained show that pure acetylene is not attacked by the chromic acid solution and that the amount of solution required for purifying the gas is dependent on the quantity of gas to be treated and amount of impurity it contains.

E. W. W.

**The Heating of, and Evolution of Chlorine from, Bleaching Powder Purifiers for Acetylene.** By FELIX B. AHRENS (*Zeit. angew. Chem.*, 1899, 777—779).—When a mixture of bleaching powder and sawdust is employed to remove the sulphur and phos

phorus compounds present as impurities in commercial acetylene, it is found that the gas, after passing through the purifiers, contains a large amount of some chlorine compound, and, moreover, after a short time, the mixture becomes strongly heated and loses its purifying properties. This result is not due to the action of acetylene on the mixture, because when bleaching powder, sawdust, and water are intimately mixed, a considerable rise of temperature occurs more or less rapidly and large quantities of chlorine and water vapour are evolved. The relationship between the composition of the mixture and the time required to reach the maximum temperature is given in a table. A similar result is obtained when sawdust is added to a cold solution of calcium hypochlorite; after a short interval, the temperature rises to  $95^{\circ}$ . No alteration of temperature is noted when pure, finely divided cellulose is substituted for sawdust. These experiments indicate that it is the lignin of the latter substance which reacts with the hypochlorite. The disadvantages attendant on the employment of sawdust may be entirely obviated by mixing the bleaching powder with some inert material, such as infusorial earth, powdered coke, brick-dust, or lead chromate. G. T. M.

**Tri- and Tetra-halogen-substituted Methanes.** By JOHN ULRICH NEF (*Annalen*, 1899, 308, 329—333. Compare Abstr., 1898, i, 102).—Alcoholic potash (1 mol.), sodium ethoxide, or potassium cyanide converts carbon tetrabromide into bromoform, but no alkali carbonate is produced; excess of alcoholic potash (6 mols.) yields carbon monoxide and ethylene, but again without production of carbonate. Carbon tetraiodide behaves in the same way, but carbon tetrachloride yields carbon monoxide and ethylic orthoformate. The behaviour of these compounds is therefore analogous to that of iodophenylacetylene; the halogen appears to assume the tervalent condition, and the resulting compound,  $CX_3 \cdot XH \cdot OEt$ , dissociates into  $CHX_3$ ,  $CHMe \cdot CHO$ , and  $HX$ . Chloropierin yields ethyl orthocarbonate when treated with sodium ethoxide, and ammonia converts it into guanidine; contrary to the statement of Bolas and Groves (*this Journal*, 1870, 23, 164; 1871, 24, 783), triphenylguanidine is not produced when aniline acts on carbon tetrabromide.

Carbon tetrabromide and finely divided silver at  $120$ — $180^{\circ}$  yield only silver bromide and carbon; bromoform under the same conditions yields no gas, but at  $200^{\circ}$  pure acetylene is evolved. Iodoform and finely divided silver at  $100^{\circ}$  in an atmosphere of carbon dioxide become ignited, and yield carbon, iodine, methane, and acetylene. When bromoform vapour is passed over strongly heated copper in an atmosphere of carbon dioxide under reduced pressure, methane is produced, and the same result attends the reduction of bromoform with zinc dust and alcohol.

Iodoform and acetone at  $135$ — $150^{\circ}$  yield the compound,  $C_5H_{11}I$ , which boils at  $74^{\circ}$  under 35 mm. pressure; an equal proportion of methylene iodide is also formed. M. O. F.

**Solid Butadiene Dibromide.** By JOHANNES THIELE (*Annalen*, 1899, 308, 333—343. Compare Abstr., 1899, i, 554).—According to the author's theory of unsaturated compounds (*loc. cit.*), butadiene,



$\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}_2$ , should yield an  $\alpha\delta$ -dibromide on direct addition of bromine; this is now found to be the case, as the initial product is the solid dibromide melting at  $53^\circ$  (compare Griner, *Abstr.*, 1893, i, 450). The constitution of the solid dibromide is established by oxidation, which converts it into  $\alpha\delta$ -dibromo- $\beta\gamma$ -dihydroxybutane; further oxidation gives rise to bromacetic acid, unaccompanied by  $\alpha\beta$ -dibromopropionic acid.

M. O. F.

**Nitrosates.** By WLADIMIR IPATIEFF (*Chem. Centr.*, 1899, ii, 178; from *J. Russ. Chem. Soc.*, 1899, 31, 441—452).—The nitrosate from  $\delta$ -methyl- $\Delta^7$ -amylene,  $\text{NO}_2\cdot\text{O}\cdot\text{CMe}_2\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\text{Me}$ , prepared by Wallach's method, crystallises from benzene, melts and decomposes at  $105^\circ$ , and after boiling with hydrochloric acid, reduces Fehling's solution; by the action of aniline dissolved in alcohol, it is converted into a crystalline compound. The nitrosate from  $\gamma$ -ethyl- $\Delta^8$ -amylene,  $\text{NO}_2\cdot\text{O}\cdot\text{CEt}\cdot\text{CMe}\cdot\text{NOH}$ , crystallises from hot benzene in prisms, melts and decomposes at  $80$ — $81^\circ$  and by the action of an alcoholic solution of aniline forms the nitrolanilide,  $\text{NOH}\cdot\text{C}_7\text{H}_{13}\cdot\text{NPh}$ ; the latter crystallises in colourless prisms, melts at  $123$ — $124^\circ$ , and is easily soluble in chloroform, ether, or hot alcohol. By the action of potassium nitrite on an acid solution of the hydrochloride, the crystalline compound,  $\text{NOH}\cdot\text{C}_7\text{H}_{13}\cdot\text{NPh}\cdot\text{NO}$ , is obtained, and by warming the hydrochloride with hydrochloric acid, a ketoanilide is formed. The nitrosate from  $\gamma$ -methyl- $\Delta^8$ -amylene,  $\text{NO}_2\cdot\text{O}\cdot\text{CMeEt}\cdot\text{CMe}\cdot\text{NOH}$ , crystallises from benzene and melts and decomposes at  $85^\circ$ . The corresponding nitrolanilide,  $\text{NOH}\cdot\text{C}_5\text{H}_{11}\cdot\text{NPh}$ , crystallises from ether or hot alcohol in large, colourless, easily soluble prisms and melts at  $78$ — $79^\circ$ . The hydrochloride,  $\text{C}_{12}\text{H}_{18}\text{ON}_2\cdot\text{HCl}$ , yields a nitroso-compound by the action of potassium nitrite, and when boiled with hydrochloric acid forms a ketoanilide.  $\Delta^8$ -Hexylene containing the group  $\cdot\text{CH}\cdot\text{CH}\cdot$  yields an oily nitrosate of sp. gr. greater than 1.

[With A. SOLONINA.]—The nitrosates of  $\Delta^8$ -amylene and  $\gamma$ -methyl- $\Delta^8$ -butylene are oils, and diamylene does not form a crystalline nitrosate. Ethyl dimethylallylmalonate which contains the group  $\cdot\text{C}\cdot\text{CH}$ , forms a nitrosate which melts at  $104$ — $105^\circ$  and after boiling with hydrochloric acid reduces Fehling's solution.

Crystalline nitrosates are obtained from compounds which contain the group  $\cdot\text{C}\cdot\text{CH}$ , and probably also from those containing the group  $\cdot\text{C}\cdot\text{C}\cdot$  (Demjanoff, *J. Russ. Chem. Soc.*, 1896, 28, 895). E. W. W.

**Hydrogenation of Allyl Alcohol.** By N. SPERANSKI (*Chem. Centr.*, 1899, ii, 181; from *J. Russ. Chem. Soc.*, 1899, 31, 423—426).—By adding aluminium shavings to a mixture of allyl alcohol with a 25 per cent. solution of potassium hydroxide and cooling the product for five days, the odour of allyl alcohol disappears and a 15 per cent. yield of normal propyl alcohol is obtained.

E. W. W.

**Simultaneous Oxidation and Hydration of Organic Compounds under the Influence of Light and Oxygen.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 627—636. Compare Richardson and Fortey, *Trans.*, 1896, 1352).—A study of chemical reactions under conditions which render them comparable with the

changes which take place in animal and vegetable organisms. Pure ether in the presence of air and water, or of air and a solution of hydrogen peroxide, suffers no change when kept in the dark. If, however, it is exposed to direct sunlight for five months, the hydrogen peroxide is completely decomposed, and the whole of the liberated oxygen as well as that of the air is absorbed, and methane, acetic acid, acetaldehyde, and ethyl alcohol are produced.

Tubes completely filled with ether, or ether and water, were exposed to sunlight for  $1\frac{1}{2}$  months; on examination, the ether was found to have suffered no change.

In 1882, several flasks were completely filled with ether and then hermetically sealed; these were opened in August, 1899, when the ether was found to be quite unchanged. A stoppered bottle which in 1882 contained pure ether, was in 1899 found to contain less than half the weight of a liquid which was free from ether, and consisted of ethyl acetate, ethyl alcohol, acetic acid, and water.

H. R. LE S.

**Dissociation of Alkyl Salts of Nitric Acid, Sulphuric Acid, and the Halogen Hydrides.** By JOHN ULRIC NEF (*Annalen*, 1899, 309, 126—189. Compare Abstr., 1898, i, 102).—As a preliminary to studying the progress of dissociation in the sugar group, the author has made a number of experiments on the behaviour of alkyl haloids towards alcoholic potash and sodium ethoxide, various salts of silver in presence of alcohol, amines, and ethyl sodiomalonate, and on the dissociation of alkyl nitrates and alkyl sulphates.

The author recognises two classes of dissociation of alkyl haloids, by which these compounds are resolved into halogen hydride, on the one hand, and either (I) a substituted methylene, such as ethylidene, or (II) an olefine, on the other. From an investigation of the behaviour of alkyl haloids towards alcoholic potash, the conclusion is drawn that, in this case, both forms of dissociation proceed simultaneously, the production of ethers depending exclusively on addition of alcohol to alkylidene. The nature of the radicles in various primary alkyl iodides,  $\text{CHRR}'\cdot\text{CH}_2\text{I}$ , exerts a remarkable influence on the proportion of one form of dissociation to the other; alkyl chlorides undergo more alkylidene dissociation than the corresponding bromides, whilst the iodides yield more olefine than the bromides. The same products are obtained when either alcoholic potash or sodium methoxide is employed, but the latter acts more slowly.

It is impossible to deal adequately with this paper in an abstract, because it is composed of the descriptions of numerous experiments with well known substances, interspersed with theoretical considerations suggested by the results.

*Tertiary butyl isocyanide*, which, according to the author's views on bivalent carbon, has the formula  $\text{CMe}_3\cdot\text{N}:\text{C}$ , is prepared from tertiary butyl iodide and silver cyanide, and boils at  $91^\circ$ ; it has a horrible smell, and is resolved by dilute acids into tertiary butylamine and formic acid.

*Tertiary butylphenylamine*,  $\text{CMe}_3\cdot\text{NHPh}$ , obtained from tertiary butyl iodide and aniline, boils at  $208\text{--}210^\circ$ .

*Benzyl nitrate*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NO}_2$ , prepared from benzyl chloride and silver nitrate, boils at  $106^\circ$  under 20 mm. pressure, and decomposes explosively at  $180$ — $200^\circ$ ; it behaves towards ethyl sodiomalonate and ethyl sodioacetoacetate like benzyl chloride, and yields dimethylbenzylammonium nitrate with dimethylaniline. M. O. F.

**Disulphones. III. Mercaptols and Disulphones of Ketonic Acids, and Unsaturated Acids derived therefrom.** By THEODOR POSNER (*Ber.*, 1899, 32, 2801—2815).—Ethyl pyruvate condenses with ethyl mercaptan in presence of hydrogen chloride to form *ethyl  $\alpha$ -diethiothiopropionate (ethyl pyruvate ethylmercaptole)*,  $\text{CMe}(\text{SEt})_2\cdot\text{CO}_2\text{Et}$ , a yellow oil which is oxidised by aqueous potassium permanganate to *ethyl  $\alpha$ -diethyldisulphonepropionate (ethyl pyruvate diethyl disulphone)*,  $\text{CMe}(\text{SO}_2\text{Et})_2\cdot\text{CO}_2\text{Et}$ ; this crystallises from 50 per cent. alcohol in long, colourless needles, melts at  $60$ — $62^\circ$ , and on hydrolysis with boiling 10 per cent. sodium hydroxide does not give rise to the corresponding acid, but loses carbon dioxide and yields diethylethylidenedisulphone,  $\text{CHMe}(\text{SO}_2\text{Et})_2$  which melts at  $75$ — $76^\circ$ , not at  $60^\circ$ , as stated by Escales and Baumann (*Abstr.*, 1887, 123).

*Ethyl  $\beta$ -diethiothiobutyrate (ethyl acetoacetate ethylmercaptole)*,  $\text{CMe}(\text{SEt})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , prepared by passing hydrogen chloride through a mixture of ethyl mercaptan and ethyl acetoacetate, is a colourless oil with a penetrating odour; it boils at  $137$ — $138^\circ$  under 37 mm. pressure, has a sp. gr. 1.0341 at  $16^\circ/13^\circ$ ,  $n_D$  1.5092 at  $15^\circ$ , and molecular refraction 86.652. It is only slowly hydrolysed by boiling 10 per cent. aqueous caustic soda, giving rise apparently to  *$\beta$ -diethiothiobutyric acid (acetoacetic acid ethylmercaptole)*,  $\text{CMe}(\text{SEt})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , but on attempting to crystallise this, ethyl mercaptan is evolved and  *$\beta$ -ethothioisocrotonic acid*,  $\text{SEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , melting at  $90$ — $91^\circ$ , formed; the latter is probably identical with the acid obtained by Autenrieth (*Abstr.*, 1890, 361) by the interaction of  *$\beta$ -chloroisocrotonic acid* with sodium ethylmercaptide, but the barium salt crystallises with  $2\text{H}_2\text{O}$ , instead of 1, as stated by that author; the ethyl ester boils at  $195^\circ$ .

*Ethyl  $\beta$ -diethiothio- $\alpha$ -methylbutyrate (ethyl methylacetoacetate ethylmercaptole)*,  $\text{CMe}(\text{SEt})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , prepared from ethyl methylacetoacetate, boils at  $132^\circ$  under 39 mm., and at  $125^\circ$  under 29 mm. pressure, and possesses a characteristic odour; it has a sp. gr. 1.0531 at  $15^\circ/13^\circ$ ,  $n_D$  at  $15^\circ$  1.51326, molecular refraction 89.662. On hydrolysis with sodium hydroxide, it yields  *$\beta$ -diethiothio- $\alpha$ -methylbutyric acid (methylacetoacetic acid ethylmercaptole)*,  $\text{CMe}(\text{SEt})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , a white powder which, on crystallising from water or acetic acid, is converted into  *$\beta$ -ethothio- $\alpha$ -methylisocrotonic acid (thioethylangelic acid)*,  $\text{SEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , which separates in white leaflets, melts at  $99$ — $101^\circ$ , and yields a crystalline barium salt,  $(\text{C}_7\text{H}_{11}\text{O}_2\text{S})_2\text{Ba} + 2\text{H}_2\text{O}$ , and an ethyl ester boiling at  $192$ — $194^\circ$ .

*Ethyl- $\beta$ -diethiothio- $\alpha$ -ethylbutyrate (ethyl ethylacetoacetate ethylmercaptole)*,  $\text{CMe}(\text{SEt})_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , prepared from ethyl ethylacetoacetate, boils at  $152^\circ$  under 49 mm., and at  $138^\circ$  under 39 mm. pressure, has a sp. gr. 1.0077 at  $16^\circ/13^\circ$ ,  $n_D$  1.49394, molecular refraction 94.70; it is hydrolysed by caustic soda only with difficulty, and is then converted

into  $\beta$ -ethothio- $\alpha$ -ethylisocrotonic acid,  $\text{SEt} \cdot \text{CMe} \cdot \text{CEt} \cdot \text{CO}_2\text{H}$ , without yielding any intermediate compound; the acid crystallises from methyl alcohol in slender, colourless needles, melts at  $64-65^\circ$ , and yields a barium salt,  $(\text{C}_8\text{H}_{13}\text{O}_2\text{S})_2\text{Ba} + 2\text{H}_2\text{O}$ .

When hydrogen chloride is passed into a solution of lævulic acid and ethyl mercaptan in glacial acetic acid,  $\gamma$ -diethothiovaleric acid (lævulic acid ethylmercaptole),  $\text{CMe}(\text{SEt})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is obtained as a colourless oil; the ethyl ester,  $\text{CMe}(\text{SEt})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , can be prepared similarly from ethyl lævulate. On oxidising the acid with cold aqueous potassium permanganate,  $\gamma$ -diethyldisulphonevaleric acid (lævulic acid diethyldisulphone),  $\text{CMe}(\text{SO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is obtained; it crystallises from alcohol in monoclinic plates, melts at  $140^\circ$ , and yields an ill-characterised barium salt, with  $4\text{H}_2\text{O}$ , and an ethyl ester,  $\text{C}_9\text{H}_{18}\text{O}_6\text{S}_2$ , which separates from dilute alcohol in large crystals and melts at  $96-96.5^\circ$ ; the latter is easily hydrolysed to the corresponding acid, without decomposing to form an unsaturated acid, as in the case of the disulphones of  $\beta$ -ketonic acids. The diethylamide,  $\text{CMe}(\text{SO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NEt}_2$ , crystallises from water in colourless plates and melts at  $101^\circ$ ; the *p*-phenetidine and the piperidide crystallise from dilute alcohol in colourless needles, melt at  $136^\circ$  and  $171^\circ$  respectively, and do not appear to possess any decided physiological activity.

$\beta$ -Diethothioylglutaric acid (acetonedicarboxylic acid ethylmercaptole,  $\text{C}(\text{SEt})_2(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$ , obtained by the slow condensation of acetonedicarboxylic acid and ethyl mercaptan at  $0^\circ$ , crystallises from dilute alcohol in large, transparent, monoclinic crystals, and melts at  $140-141^\circ$ ; the diethyl ester,  $\text{C}(\text{SEt})_2(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$ , prepared from ethyl acetonedicarboxylate, is a nearly colourless oil with a penetrating odour; it boils at  $192^\circ$  under 30 mm. pressure, has a sp. gr. 1.1012 at  $17/13^\circ$ ,  $n_D$  at  $15^\circ$  1.5051, molecular refraction 100.21. On hydrolysis with 20 per cent. aqueous caustic soda, this does not yield the corresponding acid, but in like manner to the derivatives of  $\beta$ -ketonic acids, gives rise to ethyl mercaptan and  $\beta$ -ethothioylglutamic acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{SEt}) \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , which crystallises from alcohol in monoclinic prisms and melts and decomposes at  $155-163^\circ$ ; the same compound is also formed by the interaction of acetonedicarboxylic acid and ethyl mercaptan in presence of hydrogen chloride if the mixture is not kept thoroughly cool; the copper salt,  $\text{C}_7\text{H}_8\text{O}_4\text{SCu}$ , the silver salt,  $\text{C}_7\text{H}_8\text{O}_4\text{SAg}$ , and the barium salt,  $\text{C}_7\text{H}_8\text{O}_4\text{SBa} + \text{H}_2\text{O}$ , were prepared. Ethyl  $\beta$ -diethyldisulphoneglutarate (ethyl acetonedicarboxylate diethyldisulphone),  $\text{C}(\text{SO}_2\text{Et})_2(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$ , obtained by oxidising the corresponding mercaptole with aqueous potassium permanganate, crystallises from 50 per cent. alcohol in slender, white needles, and melts at  $104^\circ$ ; on hydrolysis with 10 per cent. aqueous sodium hydroxide, it yields ethylsulphinic acid, ethyl alcohol, and  $\beta$ -ethylsulphoneylglutamic acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{SO}_2\text{Et}) \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , which forms slender needles and melts at  $175-177^\circ$ . This behaviour is similar to that of the esters of  $\beta$ -disulphonecarboxylic acids on hydrolysis (Autenrieth, Abstr., 1891, 1067); an attempt to obtain  $\beta$ -diethylsulphoneglutarate by carefully oxidising the corresponding mercaptole failed.

W. A. D.

**Resolution of Racemic Compounds into their Active Components.** By PAUL WALDEN (*Ber.*, 1899, 32, 2703—2706. Compare Marekwald and McKenzie, *Abstr.*, 1899, ii, 733).—*a*-Bromopropionyl bromide, when treated with  $\frac{1}{2}$  mol. of *l*-amyl alcohol, gives an amyl bromopropionate which has  $a_D + 3.20$ , in a 10 cm. tube, whilst when 4 mols. are used, the rotation is  $a_D + 2.99$ ; in the former case, it is supposed that the ester of the racemic bromopropionic acid is mixed with a certain amount of that of the *d*-acid, showing that the acid had been partially resolved by fractional esterification. Similarly, silver methylsuccinate with  $\frac{1}{3}$  mol. of active amyl iodide gave an ester which has  $a_D + 1.50$  in a 10 cm. tube, whilst with an excess of the iodide  $a_D + 3.50$  is obtained; in the former case, it is supposed that the product contained an excess of the ester of the *l*-acid, a conclusion which was confirmed by the fact that on hydrolysis an alkaline solution of methylsuccinic acid was obtained which showed a very slight levorotatory power. T. M. L.

**Affinity Coefficients of Saturated Fatty Acids.** By JEAN BILLIETZ (*Monatsh.*, 1899, 20, 666—678).—The conductivity of a number of fatty acids has been determined in order to see what influence structure has on the relative strength.

The following are the constants for the valeric acids:

	Normal valeric acid.	Isovaleric acid.	$\alpha$ -Methylbutyric acid.	$\alpha\alpha$ -Dimethylpropionic acid.
Boiling point.	186°	176°	177°	164°
Solubility at 25° .....	1:23.8	1:19.6	1:20.4	1:43.2
Specific gravity at 25°	0.9379	0.926	0.9433	(at 50°) 0.905
Specific volume at 25°	108.77	110.1	108.14	(at 50°) 111.5
Conductivity.....	0.00161	0.00173	0.00168	0.000978

The ratio of the conductivities corresponds neither with that of the boiling points nor yet with that of the specific volumes. The constants obtained by the inversion of sugar by these acids are in the same ratio, namely: 1:1.15:1.08:0.65.

The conductivity of normal butyric acid is 0.00154, of isobutyric acid, 0.00162, of normal hexoic acid, 0.00146, of isohexoic acid, 0.00153, of  $\alpha$ -ethylpropionic acid, 0.00203, of  $\alpha\alpha$ -dimethylpropionic acid, 0.000957.

From these results, it would appear that in a "series of isomeric acids, the conductivity depends on the proximity of the hydrogen atoms to the carboxylic group." R. H. P.

**Water of Crystallisation in the Calcium and Barium Salts of  $\gamma$ -Methylvaleric (Isohexoic) Acid.** By FRITZ ORNSTEIN (*Monatsh.*, 1899, 20, 661—665).—Saturated solutions of calcium and barium isohexoates were shaken with an excess of the salts at different constant temperatures for about 2 hours. The undissolved salt was then filtered off, quickly pressed, and analysed. The calcium salt at 0° and 13° contains  $5H_2O$ , at 20°, 40°, and 52°  $3\frac{1}{2}H_2O$ , and at 80° only  $2H_2O$ . Similarly, the barium salt at 0°, 13°, 30°, 60°, and 80° contains respectively 4, 4, 3,  $2\frac{1}{2}$ , and  $2H_2O$ . R. H. P.

**Mixed Anhydrides of Acyclic and Cyclic Acids.** By AUGUSTE BÉNAL (*Compt. rend.*, 1899, **129**, 681—684. Compare Abstr., 1899, i, 734).—Acetic isovaleric anhydride, prepared by Gerhardt's or Autenrieth's method (Abstr., 1888, 250), is never quite pure, because it is slowly decomposed by the liquid used in washing it; if the washing is continued, it is finally completely decomposed, leaving isovaleric anhydride.

A solution of 1 mol. of benzoic anhydride in 1 mol. of acetic anhydride is rapidly decomposed in the cold by an aqueous solution of sodium carbonate, leaving the benzoic anhydride unchanged. A solution of sodium carbonate has very little action on acetic benzoic anhydride. This proves that mixed anhydrides are compounds, and not mixtures, as supposed by Rousset (Abstr., 1895, i, 592).

When molecular quantities of acetic anhydride and benzoic anhydride are boiled for 3 hours, 30 per cent. of the mixture is converted into the mixed anhydride. If the heating is continued, the amount of mixed anhydride does not increase, but diminishes slightly. This accounts for the presence of free benzoic anhydride in acetic benzoic anhydride.

When acetic benzoic anhydride or acetic isovaleric anhydride is treated with ammonia, the amide formed is that of the acid which contains the least amount of carbon. This is in direct contradiction to Autenrieth's statement.

When mixed anhydrides of acetic acid and another acid are treated with phenylhydrazine, the hydrazide of acetic acid is always formed.

When molecular quantities of an alcohol and a mixed anhydride are heated together, the ester formed is that of the acid containing the smallest amount of carbon. A small amount of the ester of the other acid is also formed, due to the presence of the free anhydride of this acid. Hydrochloric acid decomposes mixed anhydrides, with formation of the chloride of the acid containing the smaller amount of carbon.

H. R. LE S.

**Vinylacetic Acid.** By FRITZ FICHTER and ALBERT KRAFFT (*Ber.*, 1899, **32**, 2799—2800. Compare Wislicenus, Abstr., 1899, i, 736).—When von Pechmann and Jenisch's  $\beta$ -hydroxyglutaric acid (Abstr., 1892, 147) is distilled under diminished pressure, the chief product is an unsaturated acid,  $C_4H_6O_2$ , together with a small amount of glutaconic acid. The acid  $C_4H_6O_2$  cannot possibly be formed by the elimination of carbon dioxide from the glutaconic acid, as this acid, when heated, yields its anhydride (Büchner, Abstr., 1894, i, 322), neither can it be formed by the elimination of water from  $\beta$ -hydroxybutyric acid, as this acid may be distilled under 12—14 mm. pressure without undergoing decomposition. The only other possibility is that an intermediate lactonic acid,  $CO \begin{array}{c} \diagup O \\ \diagdown CH_2 \end{array} CH \cdot CH_2 \cdot CO_2H$ , is formed which immediately loses water, yielding vinylacetic acid. So far, the isolation of this intermediate lactone has not been accomplished, and no direct proof of the constitution of the unsaturated acid has been obtained. It is a hygroscopic liquid boiling at  $168^\circ$  under atmospheric, or at  $70-71^\circ$  under 12—14 mm. pressure.

A calcium salt,  $(C_4H_5O_2)_2Ca + H_2O$ , is deposited from hot solutions, and this agrees with the salt described by Wislicenus (*loc. cit.*). A calcium salt containing  $2H_2O$  is deposited from cold solutions, a barium salt, with  $2H_2O$ , and a silver salt, have also been prepared.

J. J. S.

**Action of Ammonia on Lactones.** By HANS MEYER (*Monatsh.*, 1899, 20, 717—733).—A critical examination of the literature of the subject, and an attempt to formulate rules for the varying action of ammonia on lactones.

In all cases where aqueous or alcoholic ammonia reacts with a lactone, an amide of a hydroxy-acid is primarily formed, but in some cases this is then transformed into an imide (lactam). The formation of these imides does not depend on the number of carbon atoms in the "lactone" ring, but on the character of the carbon atom to which is attached the hydroxyl group of the corresponding hydroxy-acid. An imide is formed when this carbon atom is (i) tertiary, (ii) secondary and unsaturated. When the hydroxyl group attached to this carbon atom forms (i) a primary alcohol, (ii) a secondary saturated alcohol, or (iii) a phenol, the amide of a hydroxy-acid is formed.

R. H. P.

**$\alpha$ -Hydroxy- $\alpha$ -methylisohexylacetic** [ **$\alpha$ -Hydroxy- $\alpha$ -dimethylheptonic**] Acid. By KARL AUWERS (*Ber.*, 1899, 32, 2573—2575).—Auden, Perkin and Rose (*Trans.*, 1899, 75, 909) have prepared  $\alpha$ -hydroxy- $\beta$ -isoamylisobutyric acid, melting at  $76^\circ$  [not  $66^\circ$ , as quoted by the author], by hydrolysing the compound obtained by the interaction of hydrogen cyanide and isoamylacetone. In conjunction with J. Reis (*Inaug. Diss. Heidelberg*, 1897), the author prepared the same acid in the same way and called it  $\alpha$ -methyl- $\alpha$ -hydroxy-isohexylacetic acid. The methyl ester,  $C_{10}H_{20}O_3$ , is a colourless, mobile liquid with a pleasant, fruity smell and boils at  $215^\circ$  under ordinary pressure, and at  $127^\circ$  under 43 mm. pressure. Attempts to convert either the acid (or the methyl ester) into the reduction product of the campholytic acids by elimination of water were unsuccessful as unsaturated compounds were invariably obtained.

T. H. P.

**Influence of the Solvent on the Constitution of Ethyl Acetoacetate and similar Substances.** By WILHELM WISLICENUS (*Ber.*, 1899, 32, 2837—2840. Compare *Abstr.*, 1896, i, 553).—Solutions of ethyl formylsuccinate, ethyl formylphenylacetate, ethyl formylmalonate, ethyl  $\alpha$ -phenylacetoacetate, and ethyl acetoacetate in methyl alcohol, ethyl alcohol, ether, or benzene were kept until a state of equilibrium between the enolic and ketonic (or aldehydic) forms had been reached. In order to compare the amount of the enolic form present in different solvents, each solution was diluted with alcohol, and the colour developed by a drop of ferric chloride solution was compared with that produced in a standard alcoholic solution. It was found that, in all cases, the amount of the enolic form was greatest in benzene and least in methyl alcohol, but that the influence of the solvent, which was very great in the case of ethyl formylsuccinate and ethyl formylphenylacetate, was much less marked in the case of the

other three esters. Quantitative measurements of the colour intensity are given in the paper. T. M. L.

**$\beta$ -Bromoglutaric Acid.** By W. SSEMENOFF (*Chem. Centr.*, 1899, ii, 28—29; from *J. Russ. Chem. Soc.*, 1899, 31, 386—394. Compare Abstr., 1899, i, 1070).—Only small yields of glutaconic acid are obtained from ethyl sodiodicarboxyglutaconate by Conrad and Guthzeit's method, but von Pechmann and Jenisch's method (Abstr., 1892, 147; compare Bolam, Proc., 1896, 184) with slight modifications proved satisfactory. By the action of hydrobromic acid on glutaconic acid,  $\beta$ -bromoglutaric acid,  $\text{CHBr}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , alone is formed. The crystalline mass so obtained contained crystals of different forms, but they all melted at 139—140, and contained about  $\frac{3}{8}\text{H}_2\text{O}$ . By boiling  $\beta$ -bromoglutaric acid with a solution of sodium carbonate ( $1\frac{1}{2}$  mols.), 80 per cent. of  $\beta$ -hydroxyglutaric acid,  $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , and a volatile, monobasic, unsaturated acid,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , are formed (compare Abstr., 1899, 866 and 867). The properties of the latter are not those of vinylacetic acid, and the calcium and barium salts prepared from it are not identical with the known barium and calcium crotonates. E. W. W.

**Esterification of Camphoric Acid. II.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1899, 20, 685—697).—The author has prepared the alkyl salts of camphoric acid by the action of the alkyl haloids on the potassium hydrogen salt and by the action of sodium ethoxide in the presence of benzene on camphoric anhydride. The methyl hydrogen salts were also prepared by Walker's method (*Trans.*, 1892, 51, 1088). A mixture of the two alkyl hydrogen salts is very difficult to separate; the separation is, however, partly successful, if the salts are treated with a very dilute solution of copper sulphate, which precipitates the "ortho"-salt only.

When potassium hydrogen camphorate is treated with methyl iodide in methyl alcoholic solution, there is formed a mixture of the "ortho"- and "allo"-methyl hydrogen salts with some of the dimethyl ester. The same products are obtained by the action of sodium methoxide on camphoric anhydride.

These results are not contrary to the author's rule for the esterification of dibasic acids (Abstr., 1895, ii, 310), since it can be assumed that the affinity constants of the two carboxylic groups do not differ much. Also the reactions do not run smoothly, since the dialkyl esters are formed at the same time. The formation of both methyl hydrogen salts by the action of sodium methoxide on camphoric anhydride is in accordance with the author's views (Abstr., 1898, i, 30). R. H. P.

**Behaviour of Malic Acid when Heated.** By PAUL WALDEN (*Ber.*, 1899, 32, 2706—2721. Compare Aberson, Abstr., 1898, i, 513).—When malic acid is heated at  $100^\circ$  during 24 hours, or at  $160^\circ$  in a vacuum during 20 minutes, it is converted into an amorphous tribasic *anhydromalic acid*,  $\text{C}_5\text{H}_4\text{O}_3(\text{CO}_2\text{H})_3$ , which is regarded as a malomalic acid formed by elimination of water between the  $\text{CO}_2\text{H}$  group of one molecule and the OH of another. When pre-



pared at  $100^{\circ}$ , the acid has  $[\alpha]_D -18.8^{\circ}$  in acetone and  $-14.0^{\circ}$  in water, but when prepared at  $160^{\circ}$ ,  $-21.4$  in acetone and  $-16.2^{\circ}$  in water. The anhydro-acid is reconverted into *l*-malic acid when heated with water in sealed tubes. When a solution in methyl alcohol is saturated with hydrogen chloride, or when the silver salt is treated with methyl iodide, dimethyl *l*-malate is produced, together with an ester,  $C_{10}H_{12}O_8$ , melting at  $101-102^{\circ}$ , and probably identical with that described by Aberson.

On heating to a higher temperature in a vacuum during a longer period, an anhydride,  $C_5H_6O_5$ , is produced which appears to be identical with Aberson's malide from the malic acid of *Crassulaceae*.

All the reactions of malic acid from *Crassulaceae* described by Aberson are given by malic acid from mountain ash berries, and the two acids only differ in that Aberson's acid is dextrorotatory; the nature of the isomerism is not yet understood. T. M. L.

**Optical Rotation of Malic Acid in the Pure State and in Solution.** By PAUL WALDEN (*Ber.*, 1899, 32, 2849—2862).—The existence of a third optically active malic acid, obtained by Aberson from *Crassulaceae* (*Abstr.*, 1898, i, 513), would necessitate an extension or abandonment of prevailing stereochemical views. In general chemical behaviour, this new modification is extremely similar to ordinary malic acid (compare preceding abstract), and the only real difference is in the amount and direction of the rotation. This being so, the author has investigated thoroughly the rotatory behaviour of natural malic acid.

At  $20^{\circ}$ , dilute solutions of malic acid are levorotatory; a 34.24 per cent. solution is inactive, and still more concentrated solutions are dextrorotatory, converging on the value  $[\alpha]_D +5.89$  at  $22^{\circ}$  for the pure acid; natural malic acid is accordingly regarded as a dextrorotatory substance at ordinary temperatures.

Active malic acid has a relatively low melting point ( $100^{\circ}$ ) and can readily be undercooled, allowing a measurement of the rotation at lower temperatures. Crystallised and dried malic acid was kept for 10 minutes at  $100-110^{\circ}$ , and had then its rotation determined, light of various wave-lengths being used. At  $90-95^{\circ}$ , for a tube length of 100 mm.,  $a_D -5.5^{\circ}$ , at  $17^{\circ}$  after slow cooling  $a_D +5.2^{\circ}$ . These values, however, were obtained only when the acid was heated for a short time at  $100^{\circ}$ . When the heating lasted 30 minutes (*A*),  $a_D$  had the following values:  $-5.0^{\circ}$  (*l* 100 mm.) at  $50^{\circ}$ ,  $-1.0^{\circ}$  at  $43^{\circ}$ ,  $+0.5^{\circ}$  at  $36^{\circ}$ ,  $+3.0^{\circ}$  at  $28^{\circ}$ . When the heating lasted  $6\frac{1}{2}$  hours (*B*), in the course of which there was no loss of weight,  $a_D -12^{\circ}$  at about  $70^{\circ}$ ,  $-5.1^{\circ}$  at  $20^{\circ}$ . A third specimen (*C*), heated for  $14\frac{1}{2}$  hours, gave  $a_D -13^{\circ}$  at about  $60^{\circ}$ , and after cooling for 2 hours in a desiccator,  $+43^{\circ}$  at  $20^{\circ}$ . The same three specimens in acetone solution gave for  $[\alpha]_D -8.1^{\circ}$ ,  $-13.8^{\circ}$ , and  $-16.2^{\circ}$  respectively, whilst dried malic acid (not previously fused) gave in acetone solution  $[\alpha]_D -7.0^{\circ}$ ; thus the levorotation increases with the duration of the heating.

These changes can be accounted for either by the formation of a new isomeric malic acid, such as that of Aberson, or by a partial dehydration,  $2CO_2H \cdot CH(OH) \cdot CH_2 \cdot CO_2H$ , passing into  $C_5H_7O_5(CO_2H)_2$ .

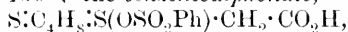
In the former case, the molecular weight and the acidity ought to be the same as those of ordinary malic acid; in the latter case, the molecular weight should be greater and the acidity less. Determinations of the molecular weight in acetone solution by the boiling point method gave for the unchanged malic acid  $M$  150—151, for  $A$  158—164, for  $B$  190—196, and for  $C$  190—198°. Equally concentrated solutions of  $A$ ,  $B$ , and  $C$  required gradually decreasing quantities of barium hydroxide for neutralisation. These observations are opposed to the assumption of a new modification of malic acid, and are well accounted for by a partial dehydration.

The rotation of natural malic acid has also been determined in numerous pure and mixed organic solvents, such as benzyl alcohol, formic acid, phenyl methyl ketone, isobutyl alcohol, acetaldehyde, and pyridine. The values obtained for  $[\alpha]_D$  in these solutions vary from  $+4.0^\circ$  to  $-30.0^\circ$ , and hence no conclusion can be drawn as to the characteristic malic acid rotation. Comparison, however, of the malic acid ion, for which  $[\alpha]_D = -14^\circ$  to  $-11^\circ$ , with the malic acid esters, for which  $[\alpha]_D = 7^\circ$  to  $-12^\circ$ , makes it tolerably certain that  $[\alpha]_D$  for the free malic acid molecule has a value of about  $-10^\circ$ . This principle of reasoning is supported by the rotations of *l*-mandelic acid (with levorotatory ion and esters), the tartaric acids, the active chlorosuccinic acids, and others. The principle, if accepted, would point to sarcosilactic acid, commonly called dextrorotatory, being really levorotatory. Similarly, *d*-glyceric acid, which yields a levorotatory ion and levorotatory esters, would have to be regarded as really levorotatory.

Discussion of the causes of the varying amount and direction of the malic acid rotation is reserved for a later paper. J. C. P.

**Diethylenedisulphidethetine.** By DANIEL STRÖMHOLM (*Ber.*, 1899, 32, 2892—2911. Compare *Abstr.*, 1898, i, 625).—*Diethylene-disulphidethetine bromide*,  $S \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained by heating together diethylene disulphide and monobromoacetic acid, crystallises in prisms melting at  $159^\circ$ ; it is readily soluble in hot water, but sparingly in cold water and alcohol. Its solution is acid and has a bitter taste; when boiled for some time, the dissolved substance undergoes a partial dissociation into its generators. *Diethylene-disulphidethetine*,  $S : C_4H_8 : S \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{CO}$ , produced by shaking the bromide with silver oxide, crystallises from water or alcohol in white needles containing  $2H_2O$ ; it melts at  $108$ — $109^\circ$ . It retains its water of crystallisation very tenaciously, and only parts with it in a vacuum desiccator; a portion of the dehydrated thetine acts catalytically on the hydrated substance, so that the latter, when mixed with the former, readily loses water even in an ordinary desiccator. The anhydrous thetine forms lustrous, white scales which decompose at about  $130^\circ$ . The compound  $(C_6H_{10}O_2S_3)_2 \cdot HBr$ , obtained by mixing together the thetine and its bromide in molecular proportion, separates in hard crystals and melts at  $179^\circ$ . The calcium and barium salts,  $(S : C_4H_8 : SBrCH_2CO_2)_2R$ , crystallise in leaflets with

$5\text{H}_2\text{O}$  and  $4\text{H}_2\text{O}$  respectively. *Diethylenedisulphidethetine chloride* resembles the bromide and melts and decomposes at  $167^\circ$ ; the *calcium* derivative crystallises with  $5\text{H}_2\text{O}$ . Ferric chloride gives a yellowish-brown precipitate with the thetine, but the product appears to be a mixture. *Diethylenedisulphidethetine iodide* forms white prisms melting at  $130^\circ$ ; the *barium* derivative crystallises with  $4\text{H}_2\text{O}$ ; the *hydrogen sulphate* forms well-defined crystals; the *nitrate* crystallises in leaflets containing  $1\text{H}_2\text{O}$ , which melt at  $109^\circ$  and the anhydrous compound melts at  $130^\circ$ ; the *benzenesulphonate*,



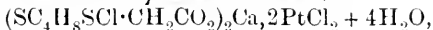
forms well-defined plates melting at  $171^\circ$ ; the *trichloroacetate* melts at  $91^\circ$ , and its *barium* salt crystallises in prisms with  $5\text{H}_2\text{O}$ , the benzoate, tartrate, and phosphates could not be obtained in a solid form; the *picrate* crystallises in tufts of yellow needles and melts at  $149^\circ$ ; the *fluoride* crystallises from a solution of hydrofluoric acid with  $2\text{H}_2\text{O}$ ; when heated to  $80^\circ$ , it loses  $1\text{H}_2\text{O}$ ; the *acetate* crystallises with  $\frac{1}{2}\text{H}_2\text{O}$ , and loses this water when left in a desiccator; the anhydrous salt melts at  $116\text{--}117^\circ$ .

*Vinylthioethylenethioglycollic acid*,  $\text{CH}_2:\text{CH}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CO}_2\text{H}$ , is obtained as an oil, together with a solid polymeride melting at  $122^\circ$ , by evaporating to dryness an alkaline solution of the thetine and liberating the products by adding a mineral acid; the *potassium* salts and *barium* salts are described.

The *platinichloride*,  $\text{PtCl}_4\cdot\text{S}:\text{C}_4\text{H}_8:\text{SCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is obtained as a yellow, amorphous precipitate on mixing solutions of platinic chloride and thetine chloride; it dissolves in caustic soda.

The *salt*,  $(\text{S}:\text{C}_4\text{H}_8:\text{SCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{K})_2\text{PtCl}_2$ , is produced by evaporating nearly to dryness an aqueous solution of thetine (2 mols.) and potassium platinosochloride (1 mol.); the oily residue is treated with alcohol, when a semicrystalline, brownish-yellow mass separates, which is pressed and dried. When allowed to remain for some time in a desiccator, this substance is converted into a yellow mass which contains no potassium; the same compound,  $(\text{S}:\text{C}_4\text{H}_8:\text{S} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CO})_2\text{PtCl}_2$ , is also formed by allowing the solution of thetine and potassium platinosochloride to remain at the ordinary temperature, or by heating it for some time on a water-bath.

*Calcium thetineplatinichloride*,  $(\text{C}_6\text{H}_{10}\text{S}_2\text{O}_2)_2\text{CaPtCl}_6$ , crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$ ; the *calcium thetine platinosochloride*,



separates in aggregates of red crystals.

*Oxydiethylenedisulphidethetine bromide*,  $\text{SO}:\text{C}_4\text{H}_8:\text{SBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is prepared by heating an aqueous solution of diethylenedisulphidethetine bromide and bromine (1 mol.) on a water-bath, and then concentrating over concentrated sulphuric acid; it crystallises in plates, melts at  $158\text{--}159^\circ$ , and is readily soluble in water.

*Oxydiethylenedisulphidethetine*,  $\text{SO}:\text{C}_4\text{H}_8:\text{S} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CO} + \text{H}_2\text{O}$ , crystallises in hard plates and melts at  $133^\circ$ ; it retains its water of crystallisation in a desiccator. The *platinichloride* crystallises, with  $4\frac{1}{2}\text{H}_2\text{O}$ , in rosettes of lustrous, orange prisms.

When an excess of bromine is added to an aqueous solution of oxydiethylenedisulphidethetine bromide, an unstable dibromo-derivative,  $\text{SO}\cdot\text{C}_4\text{H}_8\cdot\text{SBr}\cdot\text{CBr}_2\cdot\text{CO}_2\text{H}$ , is probably formed, and this, on heating the solution, decomposes into carbon dioxide and *oxydiethylene-disulphidedibromomethylsulphine bromide*,  $\text{SO}\cdot\text{C}_4\text{H}_8\cdot\text{SBr}\cdot\text{CHBr}_2$ ; this crystallises in aggregates of prisms or needles and melts at  $135^\circ$ ; the *chloride* melts at  $156^\circ$  and yields a sparingly soluble *platinichloride*. The *nitrate* is, unlike the halogen salts, very soluble.

*Dimethyldibromomethylsulphine bromide* is the final product of the action of bromine on aqueous solutions of dimethylthetine bromide; it crystallises from water in well-defined, hexagonal plates and melts at  $120$ – $121^\circ$ ; the *platinichloride* crystallises in needles.

*Dimethyldichloromethylsulphine platinichloride*,  $\text{C}_6\text{H}_{14}\text{Cl}_{10}\text{S}_2\text{Pt}$ , crystallises in lustrous scales.  
G. T. M.

**History of Thioacetaldehydes.** By EMIL FROMM (*Ber.*, 1899, 32, 2650–2653. Compare Klinger, *Abstr.*, 1899, i, 859).—Priority as regards the preparation of trithioacetaldehydes, and also as regards their constitution, is conceded to Klinger, but this author's statement that Baumann and Fromm have brought forward no fresh evidence in support of the constitution of these compounds is incorrect. The formation of trisulphones is certainly an argument in favour of the cyclic formula.

Klinger's "alloergatia" theory is criticised.

J. J. S.

**Action of Nitrosyl Chloride on Organic Compounds containing a Double Linking.** By WLADIMIR IPATIEFF (*Chem. Centr.*, 1899, ii, 176–178; from *J. Russ. Chem. Soc.*, 1899, 31, 426–441).—The action of nitrosyl chloride on compounds containing the group  $\text{:C:CH}$ ,  $\cdot\text{CH:CH}$ , or  $\cdot\text{CH:CH}_2$  respectively has been investigated. In accordance with Wallach's results, compounds of the first class were found to yield solid products. By adding fuming hydrochloric acid drop by drop to a cooled solution of  $\delta$ -methyl- $\Delta^2$ -amylenes (*Abstr.*, 1899, i, 469) in amyl nitrite and allowing the mixture to remain 24 hours, the mass solidifies and *ethylchlorisopropylketoxime*,  $\text{CMe}_2\text{Cl}\cdot\text{CEt}\cdot\text{NOH}$ , is obtained; it crystallises from benzene or ethyl acetate in colourless prisms, melts at  $77$ – $78^\circ$ , and is readily soluble in benzene. *Chlorodiethylacetoxime*,  $\text{CEt}_2\text{Cl}\cdot\text{CMe}\cdot\text{NOH}$ , prepared by the action of nitrosyl chloride on  $\gamma$ -ethyl- $\Delta^2$ -amylenes crystallises from hot ethyl acetate in prisms and melts at  $57$ – $59^\circ$ . *Chloromethylethylacetoxime*,

$\text{CMeEtCl}\cdot\text{CMe}\cdot\text{NOH}$ ,

obtained similarly from  $\gamma$ -methyl- $\Delta^2$ -amylenes, melts at  $66$ – $67^\circ$ . Since diamylene, like  $\Delta^2$ -hexylene, when treated with nitrosyl chloride, does not form a solid product, it probably does not contain the group  $\text{:C:C:}$  or  $\text{:C:CH}$  (compare Butlerow, *J. Russ. Chem. Soc.*, 9, 76). The  $\Delta^2$ -hexylene (*Annalen*, 1865, 135, 141) contained a small quantity of butylethylene (Wagner, *Diss.*). Diamylene, prepared by the action of sulphuric acid on dimethylethylcarbinol, boils at  $154$ – $156^\circ$ .

[With A. SOLOVINA].—By the action of nitrosyl chloride on isoamylenes ( $\gamma$ -methyl- $\Delta^2$ -butylene) prepared by Wischnegradski's method by the action of an alcoholic solution of an alkali on fermentation amylic iodide, only liquid products are formed.

*Action of nitrosyl chloride on disubstituted ethyl allyl ethers.* The ketonic alcohol,  $\text{CMe}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{OEt}$ , prepared from ethyl dimethylallyl ether, separates from ethyl acetate in colourless crystals and melts at  $79.5-80.5^\circ$ . Ethyl diethylallyl ether forms the compound  $\text{CEt}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{OEt}$ , which crystallises in colourless prisms and melts at  $88-89^\circ$ . From ethyl methylethylallyl ether, the compound  $\text{CMeEtCl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{OEt}$  is obtained; it melts at  $67-69^\circ$ .

*Action of nitrosyl chloride on disubstituted ethyl allylmalonates.* Ethyl dimethylallylmalonate and ethyl diethylallylmalonate form the compounds  $\text{CMe}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$  and  $\text{CEt}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$

respectively. The former crystallises from benzene in prisms and melts at  $85-87^\circ$ ; the latter crystallises from ethyl acetate in prisms and melts at  $94-96^\circ$ .

All the preceding compounds, after boiling with hydrochloric acid, reduce Fehling's solution. Crystalline chloroisnitroso-compounds are thus only obtained from compounds which contain the group  $\text{:C:CH}_2$ , and this also applies to the terpenes. The action of nitrosyl chloride is characteristic and requires little material. E. W. W.

**Electrolysis of Solutions of Sucrosé.** By KARL ULSCH (*Zeit. Elektrochem.*, 1899, 5, 539-541).—Dilute solutions of sucrose in moderately concentrated solutions of sulphuric acid, or potassium or barium hydroxide, are electrolysed at various temperatures, using platinum electrodes. With sulphuric acid alone, it is not possible to oxidise the sugar completely to carbon dioxide, but in presence of manganous sulphate the oxidation may reach 98 per cent. With potassium hydroxide, over 96 per cent. of the theoretical amount of carbon dioxide was obtained. With barium hydroxide at  $80^\circ$ , the oxidation was fairly complete in about 4 hours, and was very readily made quantitative by acidifying and adding potassium permanganate, which was not the case with the solutions in sulphuric acid or potassium hydroxide. T. E.

**Methylene-glucose from Glucose, Formaldehyde, and Hydrochloric Acid: A New Glucoside.** By BERNHARD TOLLENS (*Ber.*, 1899, 32, 2585-2588).—*Methylene-glucose*,  $\text{CH}_2\cdot\text{C}_6\text{H}_{10}\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$ , is obtained by allowing a mixture of dextrose, 40 per cent. formaldehyde solution, and hydrochloric and acetic acids to remain for some months with occasional shaking; it crystallises from water in white needles and becomes anhydrous when dried at  $100^\circ$ ; it melts at  $187-189^\circ$ , sintering at  $179-180^\circ$ . Methylene-glucose is dextrorotatory,  $[\alpha]_D +9.4^\circ$ ; it reduces Fehling's solution, one molecule requiring  $1\frac{1}{2}$  atoms of oxygen, whilst one molecule of dextrose requires  $2\frac{1}{2}$  atoms; unlike dextrose, it is not fermentable. The molecular weight was confirmed by cryoscopic determinations. The *osazone* separates from dilute alcohol as a pale yellow powder, and melts at  $164-167^\circ$ , sintering at  $150-160^\circ$ . G. F. M.

**Stereochemistry of Nitrogen.** By J. ACHILLE LE BEL (*Compt. rend.*, 1899, 129, 548-550).—The fact that Marekwald (*Abstr.*, 1899, i,

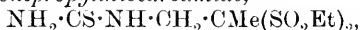
326) has been unable to confirm the author's preparation of an optically active substance by the action of moulds on the salts of methyl-ethylpropylisobutylammonium is attributed to neglect of various precautions to be observed in the preparation of this base and culture of the mould in it; full details of these are given in the paper. Repeated experiments have shown the correctness of the views put forward by the author in 1890 and 1891. N. L.

**Attempts to prepare a Diaminovaleric Acid.** By OSKAR EMMERLING (*Ber.*, 1899, 32, 2682—2685).—When  $\gamma\delta$ -Dibromovaleric acid (Messerschmidt, *Abstr.*, 1882, 35) was heated with concentrated ammonia in a sealed tube during 6 hours at  $100^\circ$ , and the ammonium salt formed converted into a lead salt which was then decomposed with hydrogen sulphide, the product obtained was not  $\gamma\delta$ -diaminovaleric acid, but 3-hydroxypiperidone,  $\text{OH}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH}\end{smallmatrix}\right\rangle\text{CO}$ , the lactam of  $\delta$ -amino- $\gamma$ -hydroxyvaleric acid; it separates from alcohol in well-formed, glistening, monoclinic crystals [ $a:c=1.1598:1$ ;  $\beta=114^\circ$ ], melts at  $145^\circ$ , has a slight sweet taste, and dissolves readily in water or alcohol; it does not combine with acids and is not acted on by nitrous acid.

*Barium  $\delta$ -amino- $\gamma$ -hydroxyvalerate* is a white, hygroscopic powder; the acid could not be isolated from it, hydroxypiperidone being at once reproduced. T. M. L.

**Disulphones. II. Aminosulphonal and its Derivatives and Homologues.** By THEODOR POSNER and JOHANNES FAHRENHORST (*Ber.*, 1899, 32, 2749—2769. Compare also *Abstr.*, 1899, i, 604).— $\beta$ -Diethyl-disulphonepropylcarbamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_2\text{Et})_2$ , prepared by the action of potassium cyanate on aminosulphonal hydrochloride, crystallises from hot water in small, white tablets melting at  $224$ — $225^\circ$ , and is readily soluble in hot water, hot alcohol, or acetic acid.

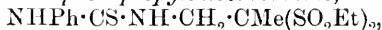
*$\beta$ -Diethyldisulphonepropylthiocarbamide,*



forms white tablets melting at  $201^\circ$ , and resembles the foregoing compound in solubility.

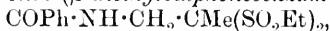
*Bis- $\beta$ -diethyldisulphonepropylthiocarbamide*,  $\text{CS}[\text{NH}\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_2\text{Et})_2]_2$ , crystallises from water in felted, microscopic needles, or from alcohol in small, quadratic tablets, and melts at  $159$ — $161^\circ$ . It is readily soluble in chloroform, acetic acid, or hot alcohol.

*Phenyl- $\beta$ -diethyldisulphonepropylthiocarbamide,*



crystallises from dilute alcohol in slender needles melting at  $173$ — $174^\circ$ , and dissolves readily in acetic acid, chloroform, hot alcohol, and hot benzene.

*Benzylaminosulphonal ( $\beta$ -diethylsulphonebenzamide),*



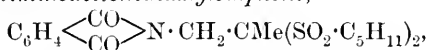
separates from hot water as an oil, which becomes crystalline when rubbed; it forms four-sided tablets with truncated angles, softens at  $96^\circ$ , and melts at  $98$ — $100^\circ$ . It dissolves readily in most of the usual media with the exception of water.

$\gamma$ -Chloro- $\beta$ -diethiothiobutane (methyl  $\alpha$ -chloroethylketone ethylmercaptole),  $\text{CHMeCl}\cdot\text{CMe}(\text{SEt})_2$ , is prepared by leading hydrogen chloride into a

cooled mixture of methyl chloroethyl ketone and ethyl mercaptan in mol. proportion; on treatment with potassium permanganate, it yields *methyl- $\alpha$ -chloroethylketonedithylsulphone*,  $\text{CHMeCl} \cdot \text{CMe}(\text{SO}_2\text{Et})_2$ , which forms small needles, melts at  $70-71^\circ$ , and dissolves readily in alcohol, chloroform, and acetic acid; like methyl  $\alpha$ -chloroethyl ketone, it does not condense with potassium phthalimide.

*Chlorodithylketonedithylsulphone*,  $\text{CHMeCl} \cdot \text{CEt}(\text{SO}_2\text{Et})_2$ , prepared in similar manner, forms a white mass, and melts at  $47-49^\circ$ .

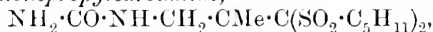
*Phthaliminoacetoneamylmercaptole*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2 \cdot \text{CMe}(\text{S} \cdot \text{C}_5\text{H}_{11})_2$ , obtained when a mixture of acetonylphthalimide and amyl mercaptan dissolved in acetic acid is saturated with hydrogen chloride, crystallises in long needles, melts at  $43-44^\circ$ , and dissolves readily in most of the ordinary media with the exception of water and cold alcohol. *Phthaliminoacetonediamylsulphone*,



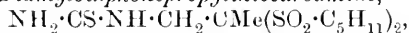
formed when the mercaptole is oxidised with potassium permanganate, crystallises from dilute alcohol in slender needles melting at  $135^\circ$ , and dissolves readily in chloroform, benzene, carbon tetrachloride, or acetone. When this substance is heated with strong potassium hydroxide solution, *potassium diamylsulphoneacetonephthalamate*,  $\text{C}_{21}\text{H}_{32}\text{O}_7\text{NS}_2\text{K}$ , is obtained in beautiful, white needles, which soften when heated, and melt at  $151-152^\circ$ ; the free acid,  $\text{CMe}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , is readily soluble in alcohol, ether, or chloroform, and melts indefinitely at  $65-70^\circ$ ; the *ammonium*, *barium*, *lead*, *cadmium*, and *silver* salts were obtained.

*Aminoacetonediamylsulphone*,  $\text{NH}_2 \cdot \text{CH} \cdot \text{CMe}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2$ , crystallises from dilute alcohol as a white mass consisting of slender needles, softens at  $80^\circ$ , melts at  $104-106^\circ$ , and dissolves readily in all the ordinary solvents excepting water. The *hydrochloride* forms slender, white needles, sinters at  $77^\circ$ , and melts at  $85-88^\circ$ ; the *platinichloride*,  $(\text{C}_{13}\text{H}_{29}\text{O}_4\text{NS}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , crystallises from dilute hydrochloric acid in yellow needles, and melts and decomposes at  $219-220^\circ$ .

*$\beta$ -Diamylsulphonepropylcarbamide*,

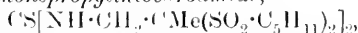


crystallises from dilute alcohol in microscopic needles melting at  $215-216^\circ$ .  *$\beta$ -Diamylsulphonepropylthiocarbamide*,



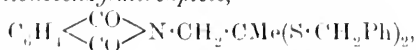
forms slender needles, sinters at  $144^\circ$ , and melts at  $148-149^\circ$ ; it dissolves readily in most media, but is sparingly soluble in water and light petroleum.

*Bis- $\beta$ -diamylsulphonepropylthiocarbamide*,



melts at  $125-126^\circ$ . *Phenyl- $\beta$ -diamylsulphonepropylthiocarbamide*,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CMe}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2$ , separates from dilute alcohol in slender needles and melts at  $154^\circ$ .

*Phthaliminoacetonebenzylmercaptole*,



separates from benzene in compact, opaque crystals melting at

137—138°. It is readily soluble in water or chloroform, and in hot benzene, alcohol, or carbon tetrachloride. *Phthaliminoacetonedibenzylsulphone*,  $C_6H_5 \cdot C_2O_2 \cdot N \cdot CH_2 \cdot CMe(SO_2 \cdot CH_2Ph)_2$ , crystallises from glacial acetic acid in slender needles melting at 244—245°, is sparingly soluble in most media, but somewhat readily soluble in hot glacial acetic acid, and readily in chloroform. When the sulphone is hydrolysed by hydrochloric acid, only a small quantity of a sulphur base is produced, and a complete breaking down appears to take place; if, however, it is heated for a short time with strong potassium hydroxide solution, and the liquid is then poured into water, a white precipitate is produced and a potassium salt remains in solution; the precipitate consists for the most part of unaltered sulphone, containing a small quantity of another substance, which may be separated by crystallisation from alcohol, and forms bundles of white crystals melting indefinitely at 85°. The filtrate from the insoluble matter, on addition of hydrochloric acid, gave a white, slimy precipitate and evolved sulphur dioxide. The precipitated acid, doubtless  $\beta$ -benzylsulphoneallylphthalamic acid,  $CH_2Ph \cdot SO_2 \cdot CMe \cdot CH \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ , produced from the sulphone by elimination of benzenesulphinic acid (compare Autenrieth, Abstr., 1891, 203 and 204), crystallised from dilute alcohol in slender, white needles melting at 193—194°, and dissolved in hot water, alcohol, or acetic acid.

$\beta$ -Benzylallylamine,  $NH_2 \cdot CH_2 \cdot C(CH_2Ph) : CH_2$ , is obtained by hydrolysing  $\beta$ -benzylsulphoneallylphthalamic acid with hydrochloric acid; it gives the isonitrile reaction, and decolorises a solution of bromine in chloroform; it has a basic odour and forms slender needles melting at 84—85°. The *hydrochloride* separates from absolute alcohol in glistening, felted needles melting at 195—200°. The *platinichloride*,  $(C_{10}H_{13}N)_2 \cdot H_2PtCl_6$ , forms granular crystals which darken at 200° and melt and decompose rapidly at 211—214°.

*Phthaliminoacetonephenylmercaptole*,  $C_6H_5 \cdot C_2O_2 \cdot N \cdot CH_2 \cdot CMe(SPh)_2$ , crystallises from benzene or dilute alcohol in slender, white needles melting at 164—165°, is readily soluble in most organic solvents, but sparingly so in water or light petroleum. *Phthaliminoacetonediphenylsulphone* crystallises from very dilute acetic acid in slender needles melting at 237—238°, is readily soluble in chloroform, hot acetic acid, or benzene, sparingly so in most other common media. When heated with strong hydrochloric acid at 180—190°, it yields a small quantity of *aminoacetonediphenylsulphone*, but is for the most part broken up into ethylenediphenylsulphone and phthalic acid; the *platinichloride* of the amino-base,  $[NH_2 \cdot CH_2 \cdot CMe(SO_2Ph)]_2 \cdot H_2PtCl_6$ , crystallises in orange-yellow needles, sinters at 135°, becomes transparent without liquefying at 150°, and decomposes at higher temperatures.

A. L.

**Cyclic Compounds. Behaviour of Cyclic Compounds at Low Temperatures.** By WLADIMIR B. MARKOWNIKOFF (*Chem. Centr.*, 1899 ii, 19; from *J. Russ. Chem. Soc.*, 1899, 31, 356—358).—Naphthenes and their derivatives may be purified by fractional freezing, the melting point being an indication of the degree of purity. When hexanaphthene, prepared from naphtha, was cooled by means of



liquid carbon dioxide, it solidified at  $-46^{\circ}$ , but after it had been separated three times by this means, it was found to solidify at  $-11^{\circ}$ . Hexanaphtheoneketone,  $C_6H_{10}O$ , solidifies at  $-45^{\circ}$  and nitrohexanaphthene at  $-34^{\circ}$ .  
E. W. W.

**Action of Zinc Methyl and Zinc Ethyl on Chlorohexanaphthene.** By N. KURSANOFF (*Ber.*, 1899, 32, 2972—2974).—When chloronaphthene,  $C_6H_{11}Cl$ , is warmed with zinc methyl, some methane is evolved, small quantities only of unsaturated compounds are formed, and *methylnaphthene* (*methylcyclohexane*),  $C_6H_{11}Me$ , is obtained in amount equal to 25 per cent. of the theoretical; this boils at  $101-102^{\circ}$  under 752 mm. pressure, has the sp. gr. 0.7804 at  $0^{\circ}/0^{\circ}$ , 0.7641 at  $20^{\circ}/0^{\circ}$ , and is converted by bromine, in the presence of aluminium bromide, into pentabromotoluene,  $C_6MeBr_5$ .

From chloro-(or iodo-)naphthene and zinc ethyl, ethane, ethylene, naphthylene,  $C_6H_{10}$ , and *ethylnaphthene* (*ethylcyclohexane*),  $C_6H_{11}Et$ , are obtained, the last in 30 per cent. yield; also a mixture of paraffins, from which one, boiling at  $242-243^{\circ}$  under 755 mm. pressure, was isolated. Ethylnaphthene boils at  $132-133^{\circ}$  under 755 mm. pressure, and has the sp. gr. 0.7913 at  $0^{\circ}/0^{\circ}$ , 0.7772 at  $20^{\circ}/0^{\circ}$ .  
C. F. B.

**Action of Bromine on Chlorobenzenes in Presence of Aluminium Chloride.** By A. MOUNEYRAT and CH. POURRET (*Compt. rend.*, 1899, 129, 605—607).—The action of bromine on chloro-derivatives in presence of aluminium chloride seems to be a general method for the preparation of chlorobromo-derivatives of cyclic hydrocarbons, all the hydrogen being displaced. For example, chlorobenzene, *p*-dichlorobenzene, 1 : 2 : 4-trichlorobenzene, and 1 : 2 : 4 : 5-tetrachlorobenzene yield chlorobromo-derivatives which sublime readily in beautiful needles and have the following melting points;  $C_6Br_5Cl$ ,  $299-300^{\circ}$ ;  $C_6Br_4Cl_2$  [ $Cl_2 = 1 : 2$ ],  $258-259^{\circ}$ ; [ $Cl_2 = 1 : 4$ ],  $278-278.5^{\circ}$ ;  $C_6Br_3Cl_3$  [ $Cl_3 = 1 : 2 : 4$ ],  $260-261^{\circ}$ ;  $C_6Br_2Cl_4$  [ $Cl_4 = 1 : 2 : 4 : 5$ ],  $246-246.5^{\circ}$ .

With a suitable proportion of bromine, this reaction affords an easy method for the preparation of *p*-chlorobromobenzene from chlorobenzene.  
C. H. B.

**Electrolytic Modification of Sandmeyer's and Gattermann's Reactions.** By EMIL VOTCEK and E. ZENÍSEK (*Zeit. Elektrochem.*, 1899, 5, 485—486).—Aniline, 30 per cent. hydrochloric acid, and sodium nitrite are mixed in the usual way; crystallised cupric chloride is then added and the solution electrolysed, a spiral of thick copper wire being used as anode, and a cylinder of sheet copper as cathode. The current density was 2.1 ampères per sq. dem., and the E.M.F. 10 volts. When the current is passed, nitrogen is given off and an oil rises to the surface; the current is stopped when nitrogen ceases to be evolved. The yield of chlorobenzene was 64 per cent. of the theoretical amount. Some azobenzene and phenol are also formed. Bromobenzene, *p*-chloro- and *o*-chloro-toluene, and  $\beta$  chloronaphthalene were made in a similar way, the yields being usually better than those obtained by the use of finely divided copper.  
T. E.

**Reduction of Nitrobenzene with Sodium.** By JULIUS SCHMIDT (*Ber.*, 1899, 32, 2911—2919).—Contrary to the statement of Hofmann and Geyger, sodium acts on nitrobenzene in ethereal solution at the ordinary temperature; when such a mixture is allowed to remain for 2 or 3 months with occasional shaking, it is found that all the sodium disappears and that a mixture of sodium oxide and disodiumphenylhydroxylamine,  $\text{NPhNa} \cdot \text{ONa}$  or  $\text{O} \cdot \text{NPhNa}_2$ , is produced. This result is obtained more rapidly by carrying out the action in boiling toluene; in both cases, excess of nitrobenzene must be employed, and it is found that 4 atoms of sodium act on one molecule of the nitro-compound (compare Löb, *Abstr.*, 1897, i, 463). Phenylhydroxylamine is obtained from the disodium compound by adding an ethereal suspension of this substance to cold normal hydrochloric acid. The mixture of disodiumphenylhydroxylamine and sodium oxide is extremely unstable, and when exposed to air in thick layers it ignites spontaneously with explosive violence. When air is passed through a well cooled ethereal suspension of the product, sodium *o*-nitrophenoxide is produced, the yield being 50 per cent. of the theoretical; when a dilute solution of chromic acid is employed as the oxidising agent, nitrosobenzene is obtained, the yield in this case being 70 per cent. Ferric chloride, mercuric chloride, bleaching powder, and nitrous acid also oxidise the disodium compound to nitrosobenzene, whilst iodine converts it into nitrosobenzene and nitrobenzene. G. T. M.

**Action of Sodium on *p*-Nitrotoluene.** By JULIUS SCHMIDT (*Ber.*, 1899, 32, 2919—2920. Compare preceding abstract).—When an ethereal solution of *p*-nitrotoluene is shaken up with sodium, *p*-azoxytoluene, *p*-azotoluene, and a dark brown, spontaneously inflammable sodium derivative are produced. When treated with hydrochloric acid, the sodium compound yields a red, amorphous substance, which is probably identical with the azoxydihydrostilbene,  $\text{O} < \begin{matrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \end{matrix}$ , investigated by Bender and Schultz (*Abstr.*, 1887, 268). G. T. M.

**Electrolytic Reduction of *m*-Nitrotoluene.** By ALBERT ROHDE (*Zeit. Elektrochem.*, 1899, 5, 322—324).—*m*-Nitrotoluene is very readily reduced by the method described by Elbs and Kopp (*Abstr.*, 1899, i, 270). The yield of *m*-azotoluene is 91 per cent. of the theoretical amount. Further reduction gives *m*-hydrazotoluene; this could not be obtained in the crystalline state, but was practically pure, for when converted into *m*-dimethylbenzidine, traces only of *m*-azotoluene were left. T. E.

**Phenylacetylene, its Salts, and Halogen Substitution Derivatives.** By JOHN ULRIC NEF (*Annalen*, 1899, 308, 264—328. Compare *Abstr.*, 1898, i, 102).—Several methods of preparing phenylacetylene are known, but the most economical consists in heating  $\omega$ -bromostyrene or crude  $\alpha$ -chlorostyrene with caustic potash (3 mols.) and a small proportion of alcohol. During the operation, phenylvinyl ethyl ether,  $\text{CHPh} \cdot \text{CH} \cdot \text{OEt}$ , is produced; it boils at  $115^\circ$  under 24 mm. pressure, and is formed when phenylacetylene is heated with alcoholic potash.

$\alpha$ -Bromostyrene,  $\text{CPhBr} \cdot \text{CH}_2$ , prepared by passing dried hydrogen

bromide into a solution of phenylacetylene in glacial acetic acid, has a sp. gr. 1.38 at 21°, and boils at 86—87° under 14 mm. pressure; it is indifferent towards sodium suspended in ether, but alcoholic sodium ethoxide regenerates phenylacetylene.

*ω*-Bromostyrene,  $\text{CHPh}:\text{CHBr}$ , obtained when the dibromide of cinnamic acid is heated with a 10 per cent. solution of sodium carbonate, has a sp. gr. 1.39 at 24.8°, and boils at 108° and 122° under pressures of 20 mm. and 36 mm. respectively; sodium wire, suspended in an ethereal solution of *ω*-bromostyrene, rapidly converts it into the sodium derivative of phenylacetylene.

*αω*-Dibromostyrene,  $\text{CBrPh}:\text{CHBr}$ , prepared from phenylacetylene and bromine in ice-cold chloroform, boils at 132—135° under 15 mm. pressure; zinc dust acts vigorously on an alcoholic solution, regenerating phenylacetylene.

The sodium derivative of phenylacetylene is a very active substance, resembling zinc ethyl in the readiness with which it becomes added to carbonyl compounds; it is produced by the action of sodium on an ethereal solution of the hydrocarbon.

*Benzoylphenylacetylene*,  $\text{CPh}:\text{C}:\text{COPh}$ , obtained on adding benzoyl chloride to the sodium derivative of phenylacetylene suspended in dried ether, crystallises from light petroleum in colourless plates melting at 49—50°, and boils at 190—200° under 15 mm. pressure; the *diiodide* melts at 148—150°. Concentrated sulphuric acid converts benzoylphenylacetylene into *α*-hydroxybenzylideneacetophenone, originally known as dibenzoylmethane (compare J. Wislicenus, this vol., i, 37). *Acetylphenylacetylene*,  $\text{CPh}:\text{C}:\text{COMe}$ , prepared from acetyl chloride and the sodium derivative of phenylacetylene, boils at 122—128° under 12 mm. pressure; concentrated sulphuric acid converts it into benzoylacetone, and ethereal iodine gives rise to the *diiodide*, which melts at 102°. Ethyl chlorocarbonate acts on the sodium derivative of phenylacetylene, forming ethyl propiolate.

*Acetophenonephenylacetylene*,  $\text{CPh}:\text{C}:\text{CMePh}:\text{OH}$ , produced when acetophenone is added to ether in which the sodium derivative of phenylacetylene is suspended, crystallises from petroleum in colourless needles and melts at 77°, boiling at 190—198° under 18 mm. pressure. *Benzophenonephenylacetylene*,  $\text{CPh}:\text{C}:\text{CPh}_2:\text{OH}$ , crystallises from a mixture of benzene and petroleum, and melts at 82°.

Dibenzoxystilbene (isobenzil),  $\text{C}_2\text{Ph}_2(\text{OBz})_2$ , prepared by the action of benzoyl chloride or benzoic anhydride on the sodium derivative of benzil, separates from ether in colourless, hemimorphic, monoclinic crystals [ $a:b:c = 0.9682:1:0.8049$ ;  $\beta = 100^\circ 34.5'$ ]. It melts at 159°. *Diacetoxystilbene*,  $\text{C}_2\text{Ph}_2(\text{OAc})_2$ , separates from ether in colourless, monoclinic crystals, and melts at 118° [ $a:b:c = 2.828:1:3.242$ ;  $\beta = 93^\circ 4'$ ]. It appears to be identical with the  $\beta$ -acetyl derivative of stilbenediol, described by Thiele (Abstr., 1899, i, 609). *Benzoylbenzhydrol*,  $\text{COPh}:\text{CPh}_2:\text{OH}$ , obtained from benzil, bromobenzene, and sodium melts at 83°; alcoholic potash resolves it into benzhydrol and benzoic acid, and its production is analogous to the formation of triphenylcarbinol from carbon monoxide, bromobenzene, and sodium (Frey, Abstr., 1896, i, 99).

In view of the properties currently ascribed to iodophenylacetylene,

the author has expressed the opinion (*loc. cit.*) that the substance belongs to the acetylidenic series; closer examination, however, has brought to light its true character as an acetylene derivative,  $\text{CPh}:\text{Cl}$ . It is most conveniently prepared by the action of iodine on the silver or sodium derivative of phenylacetylene, and forms a colourless oil having a sweet odour; it boils at  $117^\circ$  under 15 mm. pressure, and has a sp. gr. 1.75 at  $23^\circ$ . A mixture of concentrated sulphuric acid with glacial acetic acid converts it into iodoacetophenone. The compound  $\text{C}_{12}\text{H}_9\text{O}_2\text{I}$ , obtained by heating iodophenylacetylene with silver acetate and glacial acetic acid, boils at  $170^\circ$  under 20 mm. pressure; concentrated sulphuric acid converts it into iodoacetophenone. The mercury derivative of phenylacetylene,  $\text{Hg}(\text{C}_6\text{H}_5)_2$ , produced on heating iodophenylacetylene with mercury, crystallises from petroleum in colourless leaflets and melts at  $125^\circ$ ; it is also formed on adding an alcoholic solution of phenylacetylene to an aqueous mixture of potassium iodide and mercuric chloride to which caustic soda has been added.

*Iodophenylacetyleneaniline*,  $\text{CPh}:\text{C}:\text{IH}\cdot\text{NHPh}$ , prepared from iodophenylacetylene and aniline, crystallises from petroleum in flat, colourless needles and melts at  $44\text{--}46^\circ$ ; when treated in ethereal solution with iodine, triiodostyrene and aniline are produced, whilst acetic anhydride gives rise to acetanilide and iodophenylacetylene. Zinc dust in alcohol converts iodophenylacetyleneaniline into aniline and phenylacetylene; when the substance is heated with ether at  $100^\circ$  during 3 hours, phenylacetylene and *p*-iodoaniline are formed. The production of iodophenylacetyleneaniline in the manner indicated is probably the first instance of a halogen atom becoming tervalent by direct addition of an amine, and it explains the fact that isocyanogen and aniline yield hydrogen cyanide and *p*-iodoaniline.

When iodophenylacetylene and ethyl malonate (2 mols.) are heated with alcoholic sodium ethoxide (1 mol.), phenylacetylene and ethyl ethanetetra-carboxylate are produced; the former is the sole product on heating the iodo-compound with alcoholic sodium ethoxide, potash, or potassium cyanide. Ethyl malonate in presence of zinc dust appears to yield ethyl styrenemalonate,  $\text{CHPh}:\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , and ethyl phenylacetylenemalonate,  $\text{CPh}:\text{C}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ . Numerous unsuccessful attempts have been made to convert iodophenylacetylene into tetralkylammonium iodides,  $\text{CPh}:\text{C}\cdot\text{NR}_3\text{I}$ , by means of tertiary amines; experiments have also been carried on with iodoallylene,  $\text{CMe}:\text{Cl}$ , a colourless, non-toxic oil, which boils at  $109\text{--}110^\circ$ , has a sp. gr. 2.08 at  $22^\circ$ , and is devoid of the disagreeable odour of acetylidenic compounds.

*$\omega$ -Dibromostyrene*,  $\text{CHPh}:\text{CBr}_2$ , prepared by the action of alcoholic potash on  $\omega$ -bromostyrene dibromide, boils at  $135\text{--}136^\circ$  under 17 mm. pressure, and has a sp. gr. 1.819 at  $22^\circ$ ; when the vapour is passed over heated copper, phenylacetylene is produced, but phenylacetylidenic is not formed.

Bromophenylacetylene,  $\text{CPh}:\text{CBr}$ , obtained from  $\omega$ -dibromostyrene or from phenylacetylene dibromide by means of alcoholic potash and by heating the silver dibromocinnamates, is a colourless, non-toxic oil having a sweet odour; it boils at  $96^\circ$  under 15 mm. pressure, and

has a sp. gr. 1.156 at 24.2°. Concentrated sulphuric acid converts it into bromoacetophenone, whilst sodium in ether gives rise to phenylacetylene; caustic potash dissolved in methyl or ethyl alcohol, and sodium ethoxide dissolved in alcohol, resolves bromophenylacetylene into phenylacetylene and phenylacetic acid. In general behaviour, bromophenylacetylene resembles the iodo-derivative; the *diiodide*,  $\text{CPh}:\text{CBr}_2\text{I}$ , crystallises from petroleum in transparent, yellow plates, and melts at 65—66°.

*Chlorophenylacetylene*,  $\text{CPh}:\text{CCl}$ , prepared from dichlorostyrene and alcoholic potash (compare Biltz, Abstr., 1897, i, 573), boils at 74° under 14 mm. pressure, and has a sweet, agreeable odour; *phenylchlorovinyl ethyl ether*,  $\text{CHPh}:\text{CCl}\cdot\text{OEt}$ , is a bye-product boiling at 129—130° under 19 mm. pressure, and yields phenylacetic acid under the influence of alcoholic potash. When chlorophenylacetylene is heated with alcoholic potash at 110—130° during 5 hours, phenylacetic acid is produced along with an oil which boils at 142—145° under 12 mm. pressure, and probably consists of chlorophenylacetylene *dialcoholate*,  $\text{CH}_2\text{Ph}\cdot\text{CCl}(\text{OEt})_2$ ; this is a fresh instance of the resemblance between the cyanohalogenes and the halogen derivatives of phenylacetylene.

*Triethyl  $\alpha$ -naphthol-2-carboxy-3-malonate*,  $\text{C}_6\text{H}_4 \begin{matrix} \text{C}(\text{OH})\cdot\text{C}\cdot\text{CO}_2\text{Et} \\ \text{CH}=\text{C}\cdot\text{CH}(\text{CO}_2\text{Et})_2 \end{matrix}$ , prepared by the action of alcoholic sodium ethoxide on chlorophenylacetylene and ethylic malonate, crystallises from alcohol in colourless needles and melts at 88—89°; ferric chloride develops a greenish-blue coloration, and phenyldiazonium chloride yields a yellow azo-derivative. Hydrolysis, followed by elimination of carbon dioxide, gives rise to 1:3-hydroxymethylnaphthalene.

Metallic copper and silver act on perbromoethylene at high temperatures, but the sole products are carbon and the metallic bromides; zinc dust and alcohol yield acetylene and bromoacetylidene. Fuming nitric acid oxidises perbromoethylene to tribromoacetic acid. Alcoholic potash converts dibromoethylene,  $\text{CBr}_2:\text{CH}_2$ , into bromoacetylidene. Iodopropiolic acid and its salts are readily changed into diiodoacetylidene and acetylene, the odour of the former becoming perceptible when the acid is recrystallised or fused, and when aqueous solutions of the salts are heated at 60—90°. Silver iodopropiolate decomposes spontaneously at the ordinary temperature, yielding diiodoacetylidene, carbon dioxide, and the silver derivative of acetylene.

When bromine acts on an aqueous solution of iodopropiolic acid, 15 per cent. of the theoretical amount of carbon dioxide is produced, along with tribromoacrylic acid, the dibromide of iodopropiolic acid, tribromoiodoethylene,  $\text{CBr}_2:\text{CBrI}$ , dibromodiiodoethylene, and tetrabromoethylene (compare Homolka and Stolz, Abstr., 1885, 1198).

M. O. F.

**Naphtha Tar.** By NICOLAI N. LJUBAVIN [with RESWJAKOFF, RUDENKO and AREFÉEFF] (*Chem. Centr.*, 1899, ii, 118; from *J. Russ. Chem. Soc.*, 1899, 31, 358—364).—The tar, which is obtained from the naphtha residues in the manufacture of illuminating gas, yields a fraction boiling at 235—245° which contains, not only benzene,

naphthalene, and anthracene, but also  $\beta$ -methylnaphthalene. From the fraction boiling at  $240\text{--}250^\circ$ , after removing the crystals formed on cooling,  $\alpha$ -methylnaphthalene was isolated. The volatile acids and phenols are not present in sufficient quantity in the tar to allow of isolation. Organic bases were obtained from the fractions boiling between  $215^\circ$  and  $256^\circ$  (compare Ljetni, *J. Russ. Chem. Soc.*, 6, I, 274; 9, I, 269; 10, I, 237. *Dingl. Pol. J.*, 239, 72; Rudnéeff, *Dingl. Pol. J.*, 239, 72; Nikiforoff, *Chem. Zeit.*, 1896, 8).

E. W. W.

**Conversion of 1:8- and 1:5-Dinitronaphthalenes into Nitronitrosonaphthols.** By CARL GRAEBE (*Ber.*, 1899, 32, 2876—2880. Compare Friedländer, *Abstr.*, 1895, i, 543).—When the 1:8- and 1:5-dinitronaphthalenes are heated at  $40\text{--}50^\circ$  with fuming sulphuric acid, they are converted into isomerides soluble in alkalis (*Chem. Centr.*, 1897, i, 728 and 1079). The compound derived from the 1:8-dinitronaphthalene is identified as being 8-nitro-1-nitroso-1-naphthol. On treatment with hot dilute nitric acid, it yields a trinitronaphthol identical with Kehrman's and Haberkant's naphthopieric acid (*Abstr.*, 1899, i, 62); the latter substance must have one of the following constitutions [ $(\text{NO}_2)_3:\text{OH} = 1:3:5:4$  or  $1:3:8:4$ ], and it follows from the authors' experiments that the latter orientation is the correct one. A direct proof that the migrating oxygen atom of the 1:8-dinitronaphthalene enters the para-position relatively to the nitroso-group is furnished by the following data. The nitronitrosonaphthol is reduced with ammonium hydrosulphide to a diamino-naphthol, whilst with tin and hydrochloric acid it yields an aminodihydroxynaphthalene; the latter compound forms a triacetyl derivative melting at  $165^\circ$ ; this substance, on hydrolysis with potash, yields acetylaminodihydroxynaphthalene, and the monacetyl compound, when oxidised with dilute sulphuric acid and dichromate, is converted into 8-acetyl-amino-1:4-naphthaquinone. That this oxidation product is really a paraquinone is shown by the fact that it does not condense with *o*-phenylenediamine. The nitronitrosonaphthol obtained from the 1:5-dinitronaphthalene when warmed with dilute nitric acid yields a trinitronaphthol [ $(\text{NO}_2)_3:\text{OH} = 1:3:5:4$ ], and is reduced by tin and hydrochloric acid to a diamino-naphthol.

G. T. M.

**Action of Benzenediazonium Chloride on Alkaline Solutions of Nitrosophenol.** By WALTHER BORSCHKE (*Ber.*, 1899, 32, 2935—2940). The action of benzenediazonium chloride on alkaline solutions of nitrosophenol is a very complicated one, and five products have hitherto been isolated; amongst these are two phenolic substances which are precipitated by passing carbon dioxide into the alkaline solution.

*Nitrosohydroxydiphenyl*,  $\text{NO}\cdot\text{C}_{12}\text{H}_8\cdot\text{OH}$  [ $\text{OH}:\text{NO} = 2:5$ ], the more soluble of these two compounds crystallises from alcohol in yellow scales and melts at  $174^\circ$ ; it readily dissolves in solutions of the caustic alkalis, giving yellowish-red solutions, and is appreciably soluble in concentrated solutions of sodium carbonate and sodium hydrogen carbonate; it gives the Liebermann nitroso-reaction. The *benzoyl*

derivative crystallises in brownish-yellow leaflets, and decomposes at  $173-174^{\circ}$ .

*Aminohydroxydiphenyl hydrochloride*, prepared by reducing the nitroso-compound with tin and hydrochloric acid, forms colourless crystals melting at  $214^{\circ}$ ; the base is obtained in the form of unstable, colourless needles; it melts at  $192^{\circ}$ .

*Diphenylquinone*,  $C_6H_3PhO_2$ , obtained by oxidising the preceding base with potassium dichromate and dilute sulphuric acid, crystallises in lustrous, brown needles and melts at  $107^{\circ}$ . By the action of reducing agents, the quinone yields a very soluble *quinol* and an intermediate compound, crystallising from dilute acetic acid in dark violet, glistening leaflets and melting at  $176-177^{\circ}$ . A *dinitro*-compound is produced by treating nitrosohydroxydiphenyl with nitric acid; it crystallises in flattened needles or rhombic prisms, and melts at  $203-204^{\circ}$ .

*Nitrosohydroxydiphenylbenzene*,  $NO \cdot C_6H_2Ph_2 \cdot OH$  [ $3Ph_2 : OH : NO = 1 : 3 : 2 : 5$ ], the second phenolic compound, is more readily precipitated by carbon dioxide than nitrosohydroxydiphenyl; it crystallises from acetic acid in olive-green leaflets and melts at  $242-244^{\circ}$ ; it gives the Liebermann reaction, and yields a *benzoyl* derivative melting at  $163-164^{\circ}$ .

*Aminohydroxydiphenylbenzene hydrochloride*, produced by reducing the preceding nitroso-compound with tin and hydrochloric acid, crystallises in colourless, silky needles, and melts at  $240^{\circ}$ ; the base crystallises from alcohol in colourless, nacreous leaflets melting at  $146-147^{\circ}$ , these turn red on exposure to light and air.

*Diphenylbenzoquinone*,  $C_6H_2Ph_2O_2$ , obtained by oxidising the preceding base, crystallises from dilute acetic acid in long, red needles, and melts at  $137-138^{\circ}$ ; the *quinol* crystallises in colourless leaflets and melts at  $177-178^{\circ}$ .

The exact constitution of the two nitroso-compounds has not been ascertained with certainty, but it seems probable that the phenyl radicles enter the ortho-positions relatively to the hydroxyl group.

G. T. M.

**Action of Bromine on *m*-Chloro-, *m*-Bromo-, and *m*-Iodoanilines.** II. By HENRY L. WHEELER and WILLIAM VALENTINE (*Amer. Chem. J.*, 1899, **22**, 266—280).—When bromine vapour (1 mol.) is led into a solution of *m*-chloroaniline in glacial acetic acid, the principal products are 3-chloro-4-bromoaniline and 3-chloro-4:6-dibromoaniline, the former predominating, whilst a small quantity only of 3-chloro-2:4:6-tribromoaniline is formed. 3-Chloro-4-bromoaniline crystallises from dilute alcohol in colourless plates, melts at  $67-68^{\circ}$ , and on eliminating the amino-group yields *o*-chlorobromobenzene (Dobbie and Marsden, *Trans.*, 1898, **73**, 255); the *hydrochloride* crystallises in colourless needles, and, when heated, blackens at  $210^{\circ}$ ; the *sulphate* forms colourless plates, whilst the *picrate* crystallises in yellow needles and melts at  $141^{\circ}$ . 3-Chloro-4-bromoacetanilide, obtained almost quantitatively on adding bromine (1 mol.) to *m*-chloroacetanilide dissolved in glacial acetic acid, melts at  $125^{\circ}$ , and, when dissolved in cold nitric acid of sp. gr. 1.52, yields 3:4:6 *chlorobromo*-

*nitroacetanilide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{ClBr} \cdot \text{NHAc}$ , which crystallises from absolute alcohol in colourless plates and melts at  $129-130^\circ$ ; 3:4:6-*chlorobromonitroaniline*, obtained from the latter, crystallises from alcohol in long, yellow needles, melts at  $202-203^\circ$ , and yields 4-*chloro-3-bromonitrobenzene* when treated with nitrous acid in alcohol. This separates from alcohol in light-yellow needles, melts at  $60^\circ$ , and, on reduction, yields 4-*chloro-3-bromoaniline*, which crystallises in colourless plates and melts at  $78^\circ$ ; the same base is also formed on reducing the product\* obtained by dissolving *o*-chlorobromobenzene in fuming nitric acid, which hence probably consists largely of 4-*chloro-3-bromonitrobenzene*. 3-*Chloro-4-bromo-2:6-dinitroaniline*, obtained by the action of nitric acid on 3-*chloro-4-bromoaniline* at  $100^\circ$ , crystallises from absolute alcohol in dark yellow prisms and melts at  $169-170^\circ$ . 3-*Chloro-4:6-dibromoaniline* crystallises from alcohol in thin, colourless plates and melts at  $79-80^\circ$ .

The action of bromine vapour (1 mol.) on *m*-bromoaniline dissolved in glacial acetic acid yields principally 3:4-dibromoaniline together with a mixture of 3:4:6-*tribromoaniline*, and, in smaller proportion, 2:3:4-*tribromoaniline*, whilst traces of 2:3:4:6-*tetrabromoaniline* are also formed. 3:4-Dibromoaniline yields a *picrate*,  $\text{C}_6\text{H}_5\text{NBr}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , which crystallises from water in yellow needles and melts at  $149^\circ$ ; the *hydrochloride* crystallises from dilute hydrochloric acid in colourless prisms and decomposes at  $220-230^\circ$ , whilst the *sulphate* forms colourless plates. 3:4:6-*Tribromoaniline* melts at  $85-86^\circ$  and yields 1:3:4-*tribromobenzene* on eliminating the amino-group; 3:4:6-*tribromoacetanilide*,  $\text{C}_8\text{H}_6\text{NOBr}_3$ , prepared from it, or by the action of bromine (1 mol.) on 3:6-dibromoacetanilide (*infra*) dissolved in glacial acetic acid, crystallises from alcohol in colourless needles and melts at  $188-189^\circ$ . 3:6-*Dibromoacetanilide*,  $\text{C}_6\text{H}_3\text{Br}_2 \cdot \text{NHAc}$ , prepared by acetylating 3:6-dibromoaniline (Meyer and Stüber, *Annalen*, 165, 180), melts at  $171-172^\circ$ . 2:3:4-*Tribromoaniline* was not isolated, but its presence in the fraction from which 3:4:6-*tribromoaniline* is obtained is proved by the formation of 1:2:3-*tribromobenzene* on treating this fraction with nitrous acid in alcohol.

The principal product of the action of bromine (1 mol.) on *m*-iodoaniline is 4:6-dibromo-3-iodoaniline; a slightly smaller amount of 4-bromo-3-iodoaniline is also formed, together with traces of 2:4:6-*tribromo-3-iodoaniline*. 4-*Bromo-3-iodoaniline* crystallises from alcohol in colourless plates, melts at  $77^\circ$ , and is also obtained by reducing 4-*bromo-3-iodonitrobenzene* melting at  $95-96^\circ$ , prepared from 6-bromo-3-nitroaniline; the *hydrochloride* crystallises from alcohol in long, slender, colourless needles, and, when heated, decomposes at about  $210^\circ$ ; the *sulphate* crystallises from dilute sulphuric acid in colourless plates, whilst the *picrate*,  $\text{C}_6\text{H}_5\text{NBrI} \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , separates from water in yellow needles and melts at  $158-159^\circ$ . 4-*Bromo-3-iodoacetanilide*, prepared from the base, crystallises from alcohol and melts at

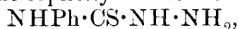
\* This nitration-product, the melting point of which, after several crystallisations, remains constant at  $49-50^\circ$ , probably consists of an isomorphous mixture of 3-bromo-4-chloro- and 3-chloro-4-bromo-nitrobenzene.—W. A. D.



138—139°. 4 : 6-Dibromo-3-iodoaniline forms long, colourless prisms, and melts at 81°. whilst 2 : 4 : 6-tribromo-3-iodoaniline crystallises from alcohol in minute, colourless prisms or plates, and melts at 115—116°. W. A. D.

**Formation of Phenylcarbylamine by the Electrolysis of Alkaline Alcoholic Solutions of Nitrobenzene and Aniline.** By JOHANN MÖLLER (*Zeit. Elektrochem.*, 1899, 5, 463—464).—A solution of nitrobenzene, caustic soda, and water in alcohol was electrolysed at 60—70° for 36 hours with a current density of 9 to 10 ampères per sq. dem. Platinum electrodes and no diaphragm were used. A strong smell of phenylcarbylamine was noticed, but the substance was not isolated. The characteristic carbylamine odour is also noticed when alkaline solutions of aniline, or of *o*-nitro- or *p*-nitro-toluene, are electrolysed. T. E.

**Action of Hydrazine on Thiocarbanilide.** By MAX BUSCH (*Ber.*, 1899, 32, 2815—2818).—Hydrazine hydrate interacts with thiocarbanilide to form varying proportions, according to the conditions, of aniline and monophenylthiosemicarbazide,



together with an *acid* containing sulphur which crystallises in prisms and melts at 205°, a *base*,  $\text{C}_{19}\text{H}_{21}\text{N}_5$ , melting at 105°, and a neutral substance free from sulphur which melts at 232°. The *base*,  $\text{C}_{19}\text{H}_{21}\text{N}_5$ , is formed almost exclusively on heating the thiocarbanilide with an excess of hydrazine hydrate and alcoholic potash for 4—5 hours at 110°, and crystallises from ether in stout, transparent needles; when heated at 180°, it loses aniline and is partially converted into the neutral substance melting at 232°; the *hydrochloride* of the base is crystalline, but rapidly decomposes, the *oxalate*,  $\text{C}_{19}\text{H}_{21}\text{N}_5 \cdot \text{C}_2\text{H}_2\text{O}_4$ , crystallises from ether in colourless prisms and melts at 160°, whilst the *picrate*,  $\text{C}_{19}\text{H}_{21}\text{N}_5 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , forms small, yellow prisms and melts at 135°. The base behaves towards aldehydes as a primary amine; the benzylidene compound could not be obtained crystalline, but the *m*-nitrobenzylidene derivative,  $\text{C}_{19}\text{H}_{19}\text{N}_5 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , separates from alcohol in canary-yellow crystals and melts at 130°. Under the influence of nitrous acid, aniline is split off from the base, and the same holds true with benzoyl chloride, benzoylaniline being formed; the base thus appears to be *trianilinomethylhydrazine*,  $\text{C}(\text{NHPh})_3 \cdot \text{NH} \cdot \text{NH}_2$ , formed by the thiocarbanilide initially undergoing resolution, under the influence of the alkali, partly into aniline, partly into carbodiphenylimide, the latter subsequently combining with hydrazine and aniline. The author intends subjecting this view to the test of experiment.

Di-*p*-chlorothiocarbanilide, under the conditions given above, does not behave like thiocarbanilide, but yields an *amino-p-chlorophenylguanidine*,  $\text{C}(\text{NH} \cdot \text{C}_6\text{H}_4\text{Cl})_2 \cdot \text{NH} \cdot \text{NH}_2$ , melting at 135°, together with a small quantity of di-*p*-chlorocarbanilide,  $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4\text{Cl})_2$ .

W. A. D.

**Chemical Composition of Norwegian Tar from Conifers.** By KNUST STRÖM (*Arch. Pharm.*, 1899, 237, 525—543).—This tar is made in the following primitive fashion. Roots of the Scotch fir (*Pinus sylvestris*) are chopped up, packed in a pit or a crevice of the rocks, and then set on fire. When the whole is well alight, turf or earth is piled over it so that but very little air can find access; at the close of the operation, the tar is ladled out from the bottom of the pit or crevice.

The tar contains volatile acids, 4.8 (calculated as acetic; nearly 9/10 were formic and acetic); phenols, 11; hydrocarbons, 61 per cent. (of these about 1/7 solid, the rest liquid). Formic, acetic, propionic, normal butyric, valeric (normal and also Renard's acid, *Ann. Chim. Phys.*, [vi], 1, 253),  $\alpha$ -methylvaleric, normal hexoic, cenanthylic, and normal octoic acids were detected, and it is probable that pelargonic, decolic, and inactive pimelic acids were also present. Of the phenols, cresol, guaiacol, creosol, ethylguaiacol, propylguaiacol, and two others of the composition  $C_{11}H_{16}O_2$  (b. p. 260—265°) and  $C_{12}H_{14}O_2$  (b. p. 300°) respectively, were detected. Amongst the hydrocarbons were terpenes and retene. The acids were separated by fractional distillation; the phenols, in the same way, combined with crystallisation of their picrates; the hydrocarbons, by distillation, combined with crystallisation of such fractions as solidified. C. F. B.

**Chloroanisidines and *m*-Chloroanisole.** By FRÉDÉRIC REVERDIN and F. ECKHARD (*Ber.*, 1899, 32, 2622—2627).—It has been shown that a migration of the halogen atom occurs when *p*-iodoanisole, *p*-iodophenetole, *p*-bromoanisole, and *p*-bromophenetole are nitrated (Abstr., 1896, i, 475; 1897, i, 27; 1898, i, 180; and 1899, i, 266); no change of this kind takes place, however, during the nitration of *o*-chloroanisole and its para-isomeride. The former substance yields *o*-chloro-*p*-nitroanisole (OMe:Cl:NO<sub>2</sub> = 1:2:4), whilst *p*-chloro-*o*-nitroanisole and a small quantity of dinitro-*p*-chlorophenol are obtained from the para-compound.

*o*-Chloro-*p*-anisidine (OMe:Cl:NH<sub>2</sub> = 1:2:4), obtained by reducing the corresponding nitro-compound with tin and hydrochloric acid, crystallises from petroleum in small, white needles melting at 62°; it is not volatile in steam. The *acetyl* derivative crystallises from water in white needles and melts at 94°; the *picrate* crystallises from dilute alcohol in yellow needles melting and decomposing at 186°.

*p*-Chloro-*o*-anisidine (OMe:Cl:NH<sub>2</sub> = 1:4:2) is soluble in the ordinary organic solvents, and crystallises in white needles melting at 82°; it is volatile in steam. The *acetyl* derivative crystallises in white needles and melts at 104°; the *picrate* forms pale yellow needles decomposing at 194°.

By reducing *m*-nitroacetyl-*o*-anisidine (OMe:NHAc:NO<sub>2</sub> = 1:2:5) with iron and acetic acid, an acetyl-diamine is produced, which is converted by the Sandmeyer reaction into *m*-chloro-*o*-anisidine; this compound is identical with the base melting at 52° obtained by Herold (Abstr., 1882, 1287) as a bye-product in the reduction of *o*-nitroanisole with tin and hydrochloric acid.

*m*-Chloroanisole, produced by eliminating the amino-group from the

preceding base, is obtained as a pale yellow oil; it boils at  $191-192^\circ$  under 728 mm. pressure, the boiling points of the ortho- and para-isomerides under this pressure being  $197-198^\circ$  and  $193-194^\circ$  respectively. The meta-compound is also prepared by substituting hydrogen for the amino-group of *m*-nitro-*o*-anisidine, reducing the nitroanisole, and finally replacing the amino-group in the resulting amine by chlorine. *m*-Chloroanisole yields a *nitro*-derivative melting at  $58^\circ$ .

*o*-Chloro-*m*-nitroanisole ( $\text{OMe}:\text{Cl}:\text{NO}_2 = 1:2:5$ ) is obtained by replacing the amino-group of *m*-nitro-*o*-anisidine by chlorine; it crystallises from petroleum in yellowish-white needles melting at  $83^\circ$ .

*o*-Chloro-*m*-anisidine ( $\text{OMe}:\text{Cl}:\text{NH}_2 = 1:2:5$ ), obtained by reducing the preceding nitro-compound, crystallises from benzene and petroleum in white needles, and melts at  $77^\circ$ ; the *acetyl* derivative crystallises in white needles and melts at  $122^\circ$ . The azo- $\beta$ -naphthol compounds of *m*-chloro-*o*-anisidine and *p*-chloro-*o*-anisidine, when developed on cotton fibre, have a brownish-violet colour resembling that of the corresponding azo-derivative of anisidine. G. T. M.

**Phenacetin.** By GEORG COHN (*Annalen*, 1899, 309, 233—238).—When phenacetin is heated with concentrated sulphuric acid, phenacetinsulphonic acid,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{NHAc}$ , is produced; the *sodium* salt crystallises from dilute alcohol in minute, white needles, and is insoluble in absolute alcohol. If 80—90 per cent. sulphuric acid is employed, ethyl acetate is eliminated from phenacetin, *p*-aminophenolsulphonic acid and *p*-aminophenol being produced. Fifty per cent. sulphuric acid converts phenacetin into the sulphate, and if the acid is boiled, acetic acid and phenetidine are produced.

Sulphonic acids have been prepared also from benzoylphenetidine, lactophenin, *p*-ethoxyphenylurethane, *p*-phenethylcarbamide, and diacetylaminophenol. M. O. F.

**Transformation of Hydroxamic Acids.** By JOHANNES THIELE and ROBERT HOWSON PICKARD (*Annalen*, 1899, 309, 189—205. Compare Thiele and Schleussner, *Abstr.*, 1897, i, 380).—The *potassium* derivative of acetylbenzhydroxamic acid crystallises in leaflets, and yields diphenylcarbamide when the aqueous solution is warmed, phenylcarbamide being obtained by the action of ammonia on dibenzhydroxamic acid and acetylbenzhydroxamic acid. An alcoholic solution of potassium dibenzhydroxamate yields diphenylcarbamide when boiled with aniline, and  $\alpha$ -phenyl- $\beta$ -phenylethylcarbamide with ethylaniline; ethylamine converts it into phenylethylcarbamide. The hydrazide of phenylcarbamic acid is produced when potassium dibenzhydroxamate is heated with hydrazine, and phenylurethane is formed on boiling an alcoholic solution of potassium acetylbenzhydroxamate or dibenzhydroxamate, methyl phenylcarbamate being formed when methyl alcohol is used.

Cinnamhydroxamic acid, prepared from ethyl cinnamate, hydroxylamine, and sodium ethoxide, crystallises from chloroform and melts at  $111.5^\circ$ . *Acetylcinnamhydroxamic acid*,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OAc}$ , obtained by the action of acetic anhydride, crystallises from benzene in colourless, lustrous plates, and melts at  $112^\circ$ ; the *potassium*

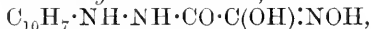
derivative decomposes in moist air. *Benzoylcinnamhydroxamic acid*,  $\text{CHPh}:\text{CH}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OBz}$ , prepared from cinnamhydroxamic acid and benzoyl chloride, crystallises from alcohol in long needles and melts at  $144^\circ$ ; the *potassium* derivative is crystalline. Amines do not convert the acylcinnamhydroxamic acids into the corresponding carbamides; Ammonia regenerates cinnamhydroxamic acid, and aniline gives rise to cinnamanilide. Boiling ethyl alcohol produces *ethyl styrylcarbamate*,  $\text{CHPh}:\text{CH}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , melting at  $89^\circ$ , and methyl alcohol generates *methyl styrylcarbamate*, which melts at  $115^\circ$ ; when these salts are hydrolysed with alcoholic potash, phenylacetaldehyde is formed.

*Dihydrocinnamhydroxamic acid*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{NOH}$ , obtained by heating ethyl dihydrocinnamate with alcoholic hydroxylamine and sodium ethoxide at  $45-50^\circ$  during four hours, crystallises from benzene in long, colourless needles and melts at  $78^\circ$ ; the *copper* derivative is insoluble in water. *Acetyldihydrocinnamhydroxamic acid*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OAc}$ , crystallises from water in lustrous plates and melts at  $99^\circ$ ; the *potassium* and *ammonium* derivatives are crystalline. *Benzoyldihydrocinnamhydroxamic acid*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OBz}$ , crystallises from alcohol in long, lustrous needles and melts at  $117^\circ$ .

*Symmetrical diphenethylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$ , prepared from the acylcinnamhydroxamic acids by warming aqueous solutions of the alkali derivatives, crystallises from dilute alcohol in large plates and melts at  $137^\circ$ ; hydrochloric acid at  $180^\circ$  resolves it into phenethylamine.

*Phenylacethydroxamic acid*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})\cdot\text{NOH}$ , produced when ethyl phenylacetate is heated with alcoholic hydroxylamine and sodium ethoxide, melts at  $121^\circ$ ; the *copper* derivative is insoluble in water. *Acetylphenylacethydroxamic acid*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OAc}$ , also melts at  $121^\circ$ , and forms a crystalline *potassium* derivative; when an aqueous solution of the latter is warmed, symmetrical dibenzylcarbamide is produced, whilst aniline converts it into symmetrical phenylbenzylcarbamide.

*a-Naphthylhydrazidoxalhydroxamic acid*,

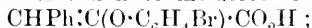


obtained from ethyl oxalate  $\beta$ -naphthylhydrazide (Freund, Abstr., 1892, 509), hydroxylamine, and sodium ethoxide, separates from alcohol in yellowish crystals, and melts at  $184.5^\circ$ , when it decomposes; the *triacetyl* derivative melts and decomposes at  $155^\circ$ .  *$\beta$ -Naphthylhydrazidoxalhydroxamic acid* melts and decomposes at  $167^\circ$ .

M. O. F.

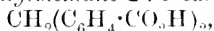
**Phenoxyacetic Acid. Bromination of Phenoxyacetic Acid.** By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1899, ii, 91-92; from *Bull. Acad. roy. Belg.*, 1899, 204-211. Compare Abstr., 1899, i, 209).—Phenoxyacetophenone,  $\text{OPh}\cdot\text{CH}_2\cdot\text{COPh}$ , obtained by the action of phenoxyacetyl chloride on benzene or of sodium phenoxide on  $\omega$ -chloroacetophenone, is a syrupy liquid and boils at  $255-257^\circ$ . Ethyl phenoxyacinnamate,  $\text{CHPh}:\text{C}(\text{OPh})\cdot\text{CO}_2\text{Et}$ , prepared by means of ethylsulphuric acid, is a syrupy liquid, boils at  $220-223^\circ$ , and is

insoluble in water. The action of bromine on this compound gave no results, but the acid forms a monobromo-derivative,



this substance crystallises from benzene, melts at  $191^\circ$ , and is identical with *p*-bromophenoxyacetic acid, obtained by heating sodium *p*-bromophenoxyacetate with benzaldehyde in presence of acetic anhydride. E. W. W.

**Diphenylmethane-2:4'-dicarboxylic Acid.** By HEINRICH LIMP-  
RICHT [and THEODOR LACH] (*Annalen*, 1899, **309**, 115—125. Compare following abstract).—*Diphenylmethane-2:4'-carboxylic acid*,



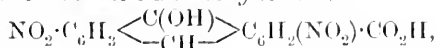
prepared by reducing benzophenone-2:4'-dicarboxylic acid with zinc dust and concentrated ammonia, contains  $11\text{H}_2\text{O}$ , and melts at  $220^\circ$ ; the *ammonium* salt melts at  $214^\circ$ , and yields diphenylmethane on distillation. The *barium* salt contains  $3\text{H}_2\text{O}$ , the *silver* salt is amorphous, and the *methylic* ester crystallises in white needles melting at  $48^\circ$ . The mixed *acetic anhydride*,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OAc})_2$ , melts at  $135^\circ$ , and loses acetic anhydride at  $140^\circ$ , but this substance is not completely removed until the temperature reaches  $280^\circ$ , when *diphenylmethane-2:4'-dicarboxylic anhydride*, melting at  $195^\circ$ , sublimes in white needles. The *chloride* melts at  $180^\circ$ , and the *amide* forms long, silky needles melting at  $236^\circ$ ; the *dianilide* melts at  $227^\circ$ , and, when boiled, yields aniline and the *anil*, which crystallises from alcohol in yellow needles and melts at  $218^\circ$ .

*Diphenylmethane diphenyl diketone*,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{COPh})_2$ , prepared by heating the chloride of diphenylmethanedicarboxylic acid with benzene and aluminium chloride, melts at  $234^\circ$ ; *diphenylmethane ditolyl diketone* crystallises from glacial acetic acid in yellow needles, and melts at  $162^\circ$ .

*9-Anthranol-2-carboxylic acid*,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{C}(\text{OH})\\ \text{CH}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ , obtained by dissolving diphenylmethanedicarboxylic acid in concentrated sulphuric acid, melts at  $305\text{--}310^\circ$ ; reduction with zinc dust and ammonia converts it into *dihydroanthracene-2-carboxylic acid*,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_2\\ \text{CH}_2\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ , which melts at  $276^\circ$ , and forms solutions exhibiting blue fluorescence.

*Anthraquinone-2-carboxylic acid*,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO}\\ \text{CO}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ , derived from anthranol-2-carboxylic acid by oxidation with potassium permanganate, crystallises from alcohol in yellow needles and melts at  $281^\circ$ .

*Dinitrodiphenylmethane-2:4'-dicarboxylic acid*,  
 $\text{CH}_2[\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CO}_2\text{H}]_2$ , prepared by dissolving diphenylmethanedicarboxylic acid in fuming nitric acid, melts at  $215^\circ$ , and when treated with concentrated sulphuric acid yields *dinitroanthranole-2-carboxylic acid*,



which crystallises from alcohol in reddish-yellow, transparent plates,

melts at  $206^{\circ}$ , and when oxidised with chromic acid is converted into *dinitroanthraquinone-2-carboxylic acid* melting at  $315^{\circ}$ .

*Diaminodiphenylmethane-2:4'-dicarboxylic acid*,



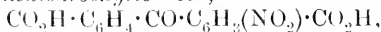
obtained by reducing the dinitro-acid with stannous chloride, melts at  $265^{\circ}$ ; the *hydrochloride* forms white plates melting at  $292^{\circ}$ , and the *sulphate* crystallises in needles. *Dihydroxydiphenylmethane-2:4'-dicarboxylic acid*,  $\text{CH}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}]_2$ , formed when nitrous acid acts on the diamino-acid, crystallises from alcohol in white needles and melts at  $236^{\circ}$ ; the *barium* salt contains  $1\text{H}_2\text{O}$ . M. O. F.

**Benzophenone-2:4'-dicarboxylic Acid.** By HEINRICH LIMP-  
RICHT (*Annalen*, 1899, 309, 96—114. Compare Abstr., 1895, i, 422).—Benzophenone-2:4'-dicarboxylic acid,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , melts at  $235^{\circ}$ . The *ammonium* salt contains  $2\text{H}_2\text{O}$ , which is removed at  $115^{\circ}$ , and the anhydrous substance melts and decomposes at  $190$ — $195^{\circ}$ ; the *barium* salt contains  $2\frac{1}{2}\text{H}_2\text{O}$ , and the *silver* salt is anhydrous. The *chloride* crystallises from benzene or ether in monoclinic prisms, and melts at  $102^{\circ}$ ; when treated with phosphorus pentachloride at  $150^{\circ}$  during several days, it yields the *tetrachloride*, which separates from benzene in yellow needles, and melts at  $198^{\circ}$ . The mixed *acetic anhydride*,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OAc})_2$ , prepared by the action of boiling acetic anhydride, crystallises from glacial acetic acid and melts at  $177^{\circ}$ ; when heated at  $180$ — $190^{\circ}$ , it yields *benzophenone-2:4'-dicarboxylic anhydride*, which is also produced on distilling the acid, and crystallises from ether in aggregates of yellow needles melting at  $184^{\circ}$ . The *amide* melts at  $285^{\circ}$ , and the *imide* at  $251^{\circ}$ , and forms a crystalline *barium* derivative; the *anilide* crystallises in needles, melts at  $210^{\circ}$ , and yields *barium* and *silver* derivatives. The *dianilide* melts at  $227^{\circ}$ . The

*4-isoxazolone*,  $\begin{array}{c} \text{CO}\cdot\text{C}_6\text{H}_4 \\ \text{O} \longrightarrow \text{N} \end{array} \geq \text{C}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , prepared by heating an alcoholic solution of benzophenonedicarboxylic acid with hydroxylamine hydrochloride, crystallises in long needles and melts at  $300^{\circ}$ ; the chloride of the acid yields, with hydroxylamine hydrochloride, the *dioxime* of the anhydride,  $\text{C}_{15}\text{H}_{10}\text{O}_4\text{N}_2$ , which melts at  $213^{\circ}$ . The *oxime* of the methyl salt melts at  $190^{\circ}$ , and the *phenylhydrazide* of the acid crystallises in white needles melting at  $253^{\circ}$ .

*Benzophenone diethyl diketone*,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{COEt})_2$ , prepared from benzophenonedicarboxylic chloride and zinc ethyl, crystallises from alcohol and melts at  $105^{\circ}$ . *Benzophenone diphenyl diketone*,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{COPh})_2$ , obtained when the chloride is heated gently with benzene and aluminium chloride, melts at  $162^{\circ}$ , and *benzophenone ditolyl diketone* gradually softens before fusion. *Benzophenonediphenyldiketonedicarboxylic acid*,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , contains  $\frac{1}{2}\text{H}_2\text{O}$ , and melts at  $185$ — $190^{\circ}$ ; the *barium* salt is a white, crystalline powder.

*Nitrobenzophenonedicarboxylic acid*,



prepared by oxidising nitro-*p*-toluoyl-*o*-benzoic acid (Abstr., 1898, i, 322), crystallises from water in aggregates of minute, colourless needles, and melts at  $230^{\circ}$ ; the *silver* salt blackens in light. M. O. F.

Mixed Methenyl Compounds. I. and II. Action of Ethyl Ethoxymethyleneacetoacetate and Ethoxymethylenemalonate on Ethyl Acetonedicarboxylate. By GIORGIO ERKERA (*Ber.*, 1899, 32, 2776—2792, 2792—2798. Compare Clausen, *Abstr.*, 1897, 1, 592).—A 72 per cent. yield of *triethyl 4-hydroxy-2-methyltrimesate*,  $\text{OEt} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Et})_3$ , is obtained when an alcoholic solution of ethyl ethoxymethyleneacetoacetate is added to an alcoholic solution of the sodium derivative of ethyl acetonedicarboxylate; it separates from light petroleum in large, non-transparent, somewhat irregular, monoclinic crystals [ $a:b:c = 1.003291:1:0.71533$ ;  $\beta = 78^\circ 22' 13''$ ]; it melts at  $47^\circ$  and dissolves readily in most organic solvents, but is insoluble in water, and its alcoholic solution gives a reddish-violet colour with ferric chloride. Its *sodium* derivative is sparingly soluble in cold alcohol, and crystallises in colourless, felted needles, which are rapidly decomposed by boiling water, yielding the *sodium diethyl* salt. *Diethyl hydroxymethyltrimesate*,  $\text{OH} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{H})(\text{CO}_2\text{Et})_2$ , crystallises from a mixture of benzene and light petroleum in colourless, monoclinic needles [ $a:b:c = 1.40879:1:0.80810$ ;  $\beta = 85^\circ 6' 52''$ ]; it melts at  $137\text{--}138^\circ$  and is readily soluble in most solvents, its alcoholic solution gives a red colour with ferric chloride, and its *barium* salt crystallises in small needles containing  $4\text{H}_2\text{O}$ . When heated, the diethyl salt yields carbon dioxide, the triethyl salt described above, and *m*-hydroxyuvitic acid, melting and decomposing at  $295\text{--}298^\circ$ , and when esterified by Fischer and Speier's method (*Abstr.*, 1896, 1, 201), it yields 15 per cent. of the triethyl ester. From this behaviour, no definite conclusion can be drawn as to the constitution of the diethyl salt by employing the Victor Meyer rule.

The *monoethyl* salt,  $\text{OH} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Et})(\text{CO}_2\text{H})_2 + \text{H}_2\text{O}$ , is obtained when the sodium derivative of the triethyl ester is boiled with an equivalent of sodium hydroxide solution and precipitated with acid; it crystallises from hot water in long, flat needles readily soluble in alcohol or ether; in the anhydrous form, it melts and decomposes at  $224^\circ$ .

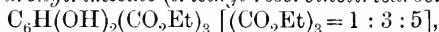
*4-Hydroxy-2-methyltrimesic acid*, obtained when any one of the three ethyl esters is boiled with an excess of alkali, crystallises from water in short, hard needles containing  $2\text{H}_2\text{O}$  and dissolves readily in alcohol. When the anhydrous acid is heated, it melts at  $257^\circ$  and evolves a gas; it then solidifies and melts a second time at  $280^\circ$ . When heated with an excess of phosphorus pentachloride and then treated with water, the original acid is obtained; all attempts to replace the phenolic OH group by chlorine were fruitless. The *mono-sodium* salt,  $\text{C}_{10}\text{H}_7\text{O}_7\text{Na} + 3\text{H}_2\text{O}$ , is sparingly soluble in water, but the di- and tri-sodium salts readily dissolve.

*Triethyl 4-ethoxy-2-methyltrimesate*,  $\text{OEt} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Et})_3$ , is a pale yellow oil which decomposes when distilled, and does not solidify in ice and salt. The *monoethyl* salt, obtained when the triethyl ester is boiled with dilute sodium hydroxide, crystallises from boiling water in prisms melting at  $195^\circ$ . Its constitution is probably [ $(\text{CO}_2\text{H})_2:\text{CO}_2\text{Et}:\text{Me}:\text{OEt} = 1:5:3:2:4$ ]. *4-Ethoxy-2-methyltrimesic acid*,  $\text{OEt} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{H})_3$ , crystallises from moderately dilute aqueous solutions in nodular masses of small needles containing  $1\text{H}_2\text{O}$ , but is

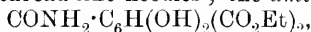
deposited from concentrated aqueous solutions as hard, anhydrous crystals melting at 242—243°.

When a cold aqueous solution of hydroxylmethyltrimesic acid is treated with slight excess of bromine water and the product recrystallised from hot benzene, small needles of 2 : 6-dibromo-3-hydroxy-4-toluic acid,  $\text{OH} \cdot \text{C}_6\text{HMeBr}_2 \cdot \text{CO}_2\text{H}$ , are deposited, whilst Claus' tri-bromometacresol (Abstr., 1889, 389) remains in solution. When the acid is brominated in acetic acid solution, the only product is the dibromohydroxytoluic acid; it crystallises from dilute alcohol in colourless needles melting at 233—234°, and is identical with the acid obtained by brominating 3-hydroxy-4-toluic acid.

*Triethyl dihydroxytrimesate (triethyl resorcinoltricarboxylate),*



is also obtained when ethyl acetonedicarboxylate is condensed with ethyl ethoxymethylenemalonate in the presence of sodium ethoxide (compare preceding page); it crystallises from alcohol in colourless needles melting at 104—105°, is readily soluble in benzene, toluene, or hot alcohol, and its alcoholic solution is turned red by ferric chloride. When boiled with sodium hydroxide (1 equivalent), it is converted into the *diethyl* salt, which crystallises from aqueous alcohol in small needles containing  $1\text{H}_2\text{O}$ ; the anhydrous compound melts at 150—151°, and is readily soluble in alcohol; the *sodium diethyl* salt,  $\text{C}_{13}\text{H}_{13}\text{O}_8\text{Na}$ , crystallises in long, thread-like needles; the *amide*,



crystallises from alcohol in colourless needles melting at 218—219°, and when hydrolysed with aqueous sodium hydroxide, is converted into the *monamide* of dihydroxytrimesic acid,  $\text{CONH}_2 \cdot \text{C}_6\text{H}(\text{OH})_2(\text{CO}_2\text{H})_2$ , which melts and decomposes at about 245°, is practically insoluble in all the ordinary organic solvents, and yields *alkali* salts which are readily soluble in water; the *barium* salt,  $\text{C}_9\text{H}_5\text{O}_7\text{N} \cdot \text{Ba} + 3\text{H}_2\text{O}$ , crystallises from water in small needles. Senhofer and Brunner's  $\alpha$ -resorcinol-dicarboxylic acid (Abstr., 1881, 265) is formed when the ethyl tricarboxylate is boiled with excess of caustic soda and mixed with a large excess of hydrochloric acid; it melts at 304—305°, not at 276°. When esterified by Fischer and Speier's method, it yields a *monoethyl* salt melting at 202—203°, together with a minute quantity of the *diethyl* ester, which crystallises in long, flat needles melting at 137°. The constitution of the dicarboxylic acid is uncertain. J. J. S.

*p*-Anisaldoximes. By HECTOR R. CARVETH (*Jour. Phys. Chem.*, 1899, 3, 437—451).—*p*-Anisaldoxime exists in two modifications, the  $\alpha$ - and  $\beta$ -forms, melting at 63° and 132° respectively, but the melting point depends on the rate of heating, being lower in each case if it is slow. This is due to tautomeric changes, and both compounds, if maintained above the melting point for some time, form a mixture with a melting point of 54.2°, which is hence the triple point, that is, the melting point of the equilibrium mixture of the two varieties. The eutectic point appears about 0.2° lower and on the side of the  $\beta$ -modification, so that the minimum melting point can only be reached by starting with the  $\beta$ -modification. The author finds that only the  $\beta$ -hydrochloride, melting at 129.5°, exists, a result at variance



with those of Hantzsch (Abstr., 1893, i, 411); by the addition of hydrogen chloride, the equilibrium temperature is raised to about  $55^{\circ}$ . In benzene and toluene solutions, the change proceeds very slowly even at the boiling point; it is never reached in aniline or alcohol solutions (compare Brühl, Abstr., 1899, i, 735). Owing to this, benzene is the best medium for separating the oximes by fractional crystallisation. The author adds examples of cases where the melting point of compounds have been stated to vary with the rate of heating, and points out that, in these cases, it is probable that isomerides may exist and are formed. L. M. J.

**Distillation of Dypnone.** By MICHEL AMEYE (*Chem. Centr.*, 1899, ii, 96—97; from *Bull. Acad. roy. Belg.*, 1899, 227—240).—Dypnone,  $\text{CMePh}\cdot\text{CH}\cdot\text{COPh}$ , is the first product of the condensation of acetophenone to form triphenylbenzene. By the action of heat on dypnone, (1) a volatile product, (2) diphenylfurfuran, and (3) triphenylbenzene are formed. According to Delacre (*Bull. Acad. roy. Belg.*, [iii], 26), the triphenylbenzene is produced by the action of styrene on diphenylfurfuran with elimination of water. The products of the reaction, however, after the acetophenone and benzaldehyde have been removed, do not yield styrene, but a hydrocarbon which combines energetically with bromine and distils at  $140$ — $165^{\circ}$ . Allylbenzene is probably present. By heating the product of the reaction at  $280^{\circ}$ , ethylbenzene is obtained. E. W. W.

**Pseudodicotoin.** By OSWALD HESSE (*Annalen*, 1899, 309, 95—96. Compare Abstr., 1895, i, 110; also Ciamician and Silber, Abstr., 1897, i, 57).—Pseudodicotoin,  $\text{C}_{25}\text{H}_{20}\text{O}_7$ , separates from a mixture of ether and petroleum in crystalline aggregates, whilst dicotoin is deposited in leaflets. When the ethereal solution is submitted to prolonged treatment with sodium carbonate, the latter dissolves cotoin, whilst the ether, on evaporation, deposits hydroxyphenylcoumalin. M. O. F.

**Condensation of Dibenzyl Ketone with Benzaldehyde.** By GUIDO GOLDSCHMIEDT and GUSTAV KNÖPFER (*Monatsh.*, 1899, 20, 734—754).—The hydrogen chloride additive product of benzylidene-dibenzyl ketone (Abstr., 1899, i, 141) easily dissolves in a strong alcoholic solution of potassium hydroxide, and on pouring this solution into water a compound,  $\text{C}_{22}\text{H}_{18}\text{O}$ , is obtained; this crystallises from alcohol in leaflets melting at  $86^{\circ}$ , does not form an additive compound with bromine, gives a deep green coloration with strong sulphuric acid, and is probably 1 : 2-diphenyltetrahydro- $\beta$ -naphthenone,  

$$\text{C}_6\text{H}_4 \begin{cases} \text{CHPh} \cdot \text{CHPh} \\ \text{CH}_2 - \text{CO} \end{cases}$$

The oxime crystallises from alcohol in prisms melting at  $158^{\circ}$ , and yields only tarry products when treated with acetic anhydride. Often, instead of the above substance, a violet coloured mass is obtained, which when washed with ether leaves an isomeric compound,  $\text{C}_{22}\text{H}_{18}\text{O}$ ; this crystallises from alcohol in needles melting at  $162$ — $163^{\circ}$ . The formation of the oxime of chlorobenzylbenzyl methyl ketone (*loc. cit.*)

requires long boiling; with only half an hour's boiling, a *compound*,  $C_{32}H_{31}O_2NCl_2$ , melting at  $130^\circ$  is obtained, which is probably an additive compound of the ketone and its oxime.

If the alkaline filtrate obtained in the preparation of 1:2-diphenyl-tetrahydro- $\beta$ -naphthenone is acidified, a monobasic *acid*,  $C_{23}H_{20}O_2$ , is precipitated; this forms lustrous leaflets melting at  $154$ — $155^\circ$ , and in neutral solution gives precipitates with solutions of silver nitrate, copper sulphate, and ferric chloride. It is saturated and forms a *methyl* ester melting at  $107^\circ$ , and an *ethyl* ester melting at  $50^\circ$ . It is probably  $\alpha\beta\gamma$ -triphenylbutyric acid.

Dibenzyl ketone can be condensed with benzaldehyde in the presence of dilute potassium hydroxide solution to form a *compound*,  $C_{29}H_{26}O_3$ ; this is very sparingly soluble in all cold, but easily soluble in most hot media, and crystallises in woolly needles melting at  $144$ — $147^\circ$ . It is probably  $\alpha\beta\delta\epsilon$ -tetraphenyl- $\gamma$ -pentanone- $\alpha\epsilon$ -diol,  $CO(CHPh \cdot CHPh \cdot OH)_3$ . It, however, does not form an oxime, and is not changed by boiling with acetic anhydride. When heated at  $150^\circ$ , benzaldehyde is eliminated and a *ketone*,  $C_{22}H_{20}O_2$ , formed; this melts at  $97^\circ$ , and is probably  $\alpha\gamma\beta$ -triphenyl- $\gamma$ -butenone- $\alpha$ -ol,  $OH \cdot CHPh \cdot CHPh \cdot CO \cdot CH_2Ph$ ; its oxime crystallises from alcohol in small needles melting at  $140^\circ$ .

R. H. P.

### Condensation Products of *o*-Aldehydic Acids with Ketones.

By HUGO LUDWIG FULDA (*Monatsh.*, 1899, 20, 698—716).—The properties of the substances obtained by Goldschmidt (*Abstr.*, 1892, 179) and Hamburger (*Abstr.*, 1899, i, 142) by the condensation of opianic acid and phthalaldehydic acid with acetone and acetophenone, have been studied, in order to determine whether they are acids or lactones. These substances are all insoluble in sodium hydrogen carbonate solution, but form salts gradually when in contact with an alkali hydroxide. According to Hantzsch's nomenclature (*Abstr.*, 1899, i, 400), they can be designated "pseudo-acids." The figures obtained by the gradual titration of phthalidedimethyl ketone, meconinedimethyl ketone, phenyl phthalidemethyl ketone, and phenyl meconinemethyl ketone with potassium hydroxide in aqueous alcoholic solution are given.

The alkali salts of these compounds were prepared by boiling them with potassium carbonate in absolute alcoholic solution until the evolution of carbon dioxide ceased, filtering, and evaporating in a desiccator. The *potassium* salt of meconinedimethyl ketone has a deep yellow colour, whilst the *potassium* salt of phenyl phthalidemethyl ketone forms long, silky needles, which are almost colourless. These salts undergo a gradual decomposition when titrated with decinormal hydrochloric acid, helianthin being used as an indicator. The investigations show that these substances possess the lactone form owing to an intramolecular transformation of the true acids, which are primarily formed in the condensation.

In order to decide whether the acids primarily formed are unsaturated acids or hydroxy-acids, the following methyl derivatives were prepared by heating the potassium salts of these substances with methyl iodide and methyl alcohol in a sealed tube: the *methyl* derivative of phthalidedimethyl ketone,  $C_{12}H_{12}O_3$ , is a yellow oil; the *methyl* derivative of

meconinedimethyl ketone,  $C_{14}H_{16}O_5$ , forms yellow needles melting at  $72-73^\circ$ ; the *methyl* derivative of phenyl phthalidemethyl ketone,  $C_{17}H_{12}O_3$ , is a yellowish oil; the *methyl* derivative of phenyl meconine-methyl ketone,  $C_{13}H_{18}O_5$ , forms yellowish needles melting at  $97-98^\circ$ . The formation of these compounds shows that the substances primarily formed in the condensations in question are unsaturated acios.

The paper concludes with a discussion of the probable formulae of some of Hamburger's compounds. R. H. P.

**Isomeric Forms of Dibenzoylmethane.** By JOHANNES WISLICENUS [with BRUNO LÖWENHEIM, PAUL SCHMIDT, and HARRY EDWARD WELLS] (*Annalen*, 1899, 308, 219—263).—When benzylideneacetophenone,  $CHPh:CH \cdot CPh$ , is dissolved in chloroform and treated with bromine (1 mol.), the *dibromide* is precipitated; this crystallises from alcohol and melts at  $156.5-157.5^\circ$ . *Bromobenzylideneacetophenone*,  $CBrPh:CH \cdot CPh$ , prepared by heating the dibromide with alcoholic potassium acetate, crystallises in slender, yellow prisms, and melts at  $43-44^\circ$ . Hot alcoholic potash converts these bromo-compounds into a mixture of two isomerides,  $C_{15}H_{12}O_2$ , of which the less readily soluble is the substance known as dibenzoylmethane (von Baeyer and Perkin, *Abstr.*, 1884, 64). Closer investigation, however, has shown that the more readily soluble isomeride is the actual dibenzoylmethane,  $CH_2(CPh)_2$ , whilst the substance hitherto known by this name is the *keto-enolic* modification, or  *$\alpha$ -hydroxybenzylideneacetophenone*,  $OH \cdot CPh:CH \cdot CPh$ ; the latter is readily produced from the former, but the converse reaction is not complete.

Dibenzoylmethane, the new compound under an old name, is obtained quantitatively by heating bromobenzylideneacetophenone with alcoholic soda (1 mol.), and melts simultaneously with the isomeride at  $77-78^\circ$ ; in chemical behaviour, it closely resembles the *keto-enolic* modification, but differs from that substance in crystalline form, and in its greater solubility in organic media. It is insoluble in caustic alkalis, and is indifferent towards ferric chloride and copper acetate, whilst  *$\alpha$ -hydroxybenzylideneacetophenone* dissolves readily in dilute alkalis, develops immediately an intense, violet-red coloration with ferric chloride, and yields, with copper acetate, a crystalline, greyish-green *copper* derivative,  $(C_{15}H_{11}O_2)_2Cu$ .

Although the isomerides are indifferent towards acetic anhydride and glacial acetic acid, phenylcarbimide combines with the *keto-enolic* modification, but not with dibenzoylmethane; the *urethane*,  $NHPh \cdot CO_2 \cdot CPh:CH \cdot CPh$ , crystallises from alcohol in minute needles and melts at  $181^\circ$ .

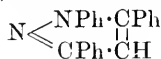
The two forms behave alike towards dilute nitric acid, yielding benzoic acid and carbon dioxide, but potassium permanganate oxidises dibenzoylmethane much more slowly than  *$\alpha$ -hydroxybenzylideneacetophenone*, benzoic and benzoylformic acids being produced.

Both modifications boil at  $219-221^\circ$  under 18 mm. pressure, without undergoing change. As already indicated, dibenzoylmethane is the more readily soluble, dissolving in 11.6 parts of alcohol at  $19.5^\circ$ , whilst  *$\alpha$ -hydroxybenzylideneacetophenone* requires 22.5 parts. Concentrated sulphuric and hydrochloric acids rapidly convert

dibenzoylmethane into the keto-enolic modification, and the same change is effected by alkalis, but in this case is attended with resolution into acetophenone and benzoic acid. The two modifications behave alike towards bromine, yielding bromodibenzoylmethane and dibromodibenzoylmethane (compare Neufville and von Pechmann, Abstr., 1891, 318).

3 : 5-Diphenylisoxazole,  $\text{CH} \begin{smallmatrix} \text{CPh} \cdot \text{O} \\ \text{CPh} \cdot \text{N} \end{smallmatrix}$ , prepared by heating alcoholic solutions of the isomerides with hydroxylamine hydrochloride, crystallises from carbon disulphide in long, six-sided prisms and melts at  $140.5-141^\circ$ ; it is indifferent towards concentrated hydrochloric acid at  $200^\circ$ , and merely volatilises when fused with moist alkali, but hydriodic acid at  $150^\circ$  attacks it slowly, forming benzoic acid. The *oxime*,  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$ , is produced when free hydroxylamine acts on an alcoholic solution of  $\alpha$ -hydroxybenzylideneacetophenone or its isomeride, and crystallises in lustrous prisms melting at  $165^\circ$ ; the *compound*,  $\text{C}_{22}\text{H}_{18}\text{O}_3\text{N}_2$ , obtained from the oxime by the action of phenylcarbimide, crystallises in needles, and melts at  $132^\circ$ .

The two modifications behave alike towards hydrazine and phenylhydrazine, yielding 3 : 5-diphenylpyrazole,  $\text{N} \begin{smallmatrix} \text{NH} \cdot \text{CPh} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix}$  (Knorr and Duden, Abstr., 1893, i, 231), and 1 : 3 : 5-triphenylpyrazole,

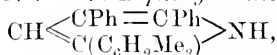


(Knorr and Laubmann, Abstr., 1888, 725), respectively. Semicarbazide converts the isomerides into the *semicarbazone* of  $\alpha$ -hydroxybenzylideneacetophenone, which crystallises in thin plates, and decomposes at  $187^\circ$ , if heated slowly, melting at  $205^\circ$  when the temperature is raised more rapidly; 3 : 5-diphenylpyrazole is produced at the same time, and also results from the semicarbazone under the influence of concentrated hydrochloric acid in alcohol. M. O. F.

**Potassium Cyanide as a Condensing Agent.** By ALEXANDER SMITH (*Amer. Chem. J.*, 1899, 22, 249-256. Compare Trans., 1890, 643).—*Desyl- $\alpha$ -acetoneaphthone*,  $\text{CPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_{10}\text{H}_7$ , prepared by boiling a solution of  $\alpha$ -acetoneaphthone and benzoin in 50 per cent. alcohol containing a small quantity of potassium cyanide for 1 hour, crystallises from benzene on adding light petroleum in stellar aggregates of white needles and melts at  $151^\circ$ ; when dissolved in concentrated sulphuric acid, it yields 2 : 3-diphenyl-5- $\alpha$ -naphthyl-furfuran,  $\text{CPh} \begin{smallmatrix} \text{CPh} \\ \text{CH} \cdot \text{C}(\text{C}_{10}\text{H}_7) \end{smallmatrix} > \text{O}$ , which crystallises from light petroleum in slender, white needles and melts at  $96^\circ$ . 2 : 3-Diphenyl-5- $\alpha$ -naphthyl-pyrrole,  $\text{CPh} \begin{smallmatrix} \text{CPh} \\ \text{CH} \cdot \text{C}(\text{C}_{10}\text{H}_7) \end{smallmatrix} > \text{NH}$ , prepared by heating the naphthone with alcoholic ammonia at  $200-220^\circ$  for 8 hours, crystallises from alcohol in white needles and melts at  $122^\circ$ ; the corresponding *thiophen* derivative, obtained by heating desyl- $\alpha$ -acetoneaphthone with phosphorus pentasulphide, melts at  $93^\circ$ .

*Desyl-β-acetonaphthone*, prepared from β-acetonaphthone, crystallises from benzene in white needles and melts at 155°.

When benzaldehyde is heated with a little powdered potassium cyanide for 3–4 hours at 150°, a good yield of benzoin is obtained; potassium hydroxide did not give benzoin by this method. Desyl-acetophenone and desyl-α-acetonaphthone, however, are easily prepared by heating benzoin and the corresponding ketone with either potassium cyanide or hydroxide at 150° for 20 minutes. Moreover, by this process, *desylacetomesitone*,  $\text{COPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Me}_3$ , which cannot be prepared by heating benzoin and acetomesitone with potassium cyanide in alcoholic solution, is readily obtained; it crystallises from alcohol in white needles, melts at 115°, and when dissolved in cold concentrated sulphuric acid yields the corresponding *furfuran* derivative which crystallises from methyl alcohol in stellar aggregates of needles and melts at 87°. 2:3-Diphenyl-5-mesitylpyrrole,



obtained by heating desylacetomesitone with alcoholic ammonia for 7 hours at 230–240°, forms white needles and melts at 188°.

The action of potassium cyanide on a fused mixture of benzyl cyanide and benzoin gives rise, not to the simple condensation product expected, but to the compound,  $\text{OH} \cdot \text{CHPh} \cdot \text{CPh}(\text{CHPh} \cdot \text{CN})_2$ , obtained by Schleussner (*Diss. Frankfurt*, 1893), on heating the same substances in alcoholic solution; α-phenylcinnamonitrile (Frost, *Abstr.*, 1889, 597) and diphenylsuccinonitrile are also formed. W. A. D.

**Preparation and Configuration of the Six Isomeric Inactive Benzylidenebisacetylacetones.** By ROBERT SCHIFF (*Annalen*, 1899, 309, 206–232).—Under conditions described in the original paper, the author has isolated the six isomeric inactive benzylidenebisacetylacetones and determined their configuration.

The *diketonic* modification,  $\text{CHPh}(\text{CHAc} \cdot \text{COMe})_2$ , crystallises from a mixture of benzene and petroleum in slender, silky needles, and melts at 163°; the alcoholic solution is indifferent towards ferric chloride, even after boiling, or after an interval of many days.

The *trans-keto-enolic* modification,  $\text{COMe} \cdot \text{CHAc} \cdot \text{CHPh} \cdot \text{CAc} \cdot \text{COMe} \cdot \text{OH}$ , obtained by repeatedly treating with boiling benzene the benzylidenebisacetylacetone (melting at 168°) described by Knoevenagel (*Abstr.*, 1895, i, 50), crystallises from benzene in leaflets, and melts at 182–183°, when it becomes deep red; the cold, alcoholic solution with ferric chloride gradually develops a red coloration, which is produced immediately when the liquid is warmed. The specimen melting at 168° obtained by Knoevenagel's method, is probably an allelotropic mixture (Knorr, *Abstr.*, 1899, i, 673) of the *trans-keto-enolic* modification with the *trans-trans-dienolic* form (see below). The *trans-keto-enolic* modification is very labile, and in the course of two months becomes converted spontaneously into the allelotropic mixture, this change being effected also by a single crystallisation from boiling alcohol.

The *cis-keto-enolic* modification crystallises from alcohol in slender, lustrous needles, and melts at 123°; the cold solution is indifferent towards ferric chloride, even after a long interval, but when boiled, at

once develops colour. It dissolves in cold, dilute caustic soda, and when the solution is acidified, a mixture of the original substance with the *cistrans*-dienolic modification is produced; an allelotropic mixture of these two forms, melting at 110—112°, is obtained on fusing the *cis*-keto-enolic derivative.

The *trans*-*trans*-*dienolic* modification,  $\text{CHPh}(\text{CHAc} \cdot \text{CMe} \cdot \text{OH})_2$ , obtained by the action of alcoholic sodium ethoxide on the *trans*-keto-enolic form, crystallises from hot petroleum in aggregates of long, colourless prisms, and melts at 91—92°, when it undergoes ketonisation in part, yielding the allelotropic mixture which melts at 168°; the alcoholic solution immediately develops a deep carmine red coloration with ferric chloride. The *anhydride*,  $\text{C}_{17}\text{H}_{18}\text{O}_3$ , is a colourless, viscous oil which is indifferent towards ferric chloride; when treated with 5 per cent. caustic soda, acetic acid is eliminated, and 5 : 3-phenylmethyl- $\Delta^2$ -cyclohexenone,  $\text{CHPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe} \\ \text{CH}_2 - \text{CO} \end{smallmatrix} \text{CH}$ , produced (compare Knoevenagel, *loc. cit.*)

The *cistrans*-*dienolic* modification prepared from the *cis*-keto-enolic derivative by the action of alcoholic sodium ethoxide, melts at 93—94° to a clear liquid which becomes turbid at 95°, and then crystalline, melting finally at 118—119°; after an interval, if allowed to cool, the same specimen melts at 110—112°, which temperature undergoes no further change, being that which the allelotropic mixture of the *cis*-keto-enolic and *cistrans*-*dienolic* derivatives undergoes fusion. Ferric chloride immediately develops an intense wine-red coloration with this form of benzylidenebisacetylacetone.

The *cis*-*cis*-*dienolic* modification occurs in the mother liquor of the initial product of the condensation of benzaldehyde with acetylacetone, and crystallises from benzene in large, lustrous prisms melting at 125—126°; it immediately develops a deep carmine-red coloration with ferric chloride. It is a stable substance, and may be heated at the melting point for some time without changing into the diketonic form melting at 163°; this conversion is brought about, however, by fuming hydrochloric acid.

Further confirmation of the proposed configuration of the isomerides is afforded by the conversion of the *cis*-keto-enolic modification into the *trans*-keto-enolic form under the influence of hot, fuming hydrochloric acid, and the transformation of diketobenzylidenebisacetylacetone into the *trans*-*trans*-*dienolic* derivative by the agency of alcoholic sodium ethoxide.

M. O. F.

Compounds from Rhubarb, and Allied Substances. By OSWALD HESSE (*Annalen*, 1899, 309, 32—75. Compare Abstr., 1895, i, 292 and 299).—By a method of treatment which is fully described in the original paper, Chinese rhubarb yields chrysophanic acid, emodin, rhabarberone, and rhein.

Chrysophanic acid,  $\text{C}_{17}\text{H}_{10}\text{O}_7$ , crystallises from benzene, alcohol, or glacial acetic acid in yellow leaflets, and melts at 186—188°; the substance has been previously described as melting at different temperatures between 154° and the true point of fusion, the presence of varying amounts of methylechrysophanic acid being the cause of the

uncertainty. It dissolves in 1989 parts of absolute alcohol at 15°, and the solution develops a dark reddish-brown coloration with ferric chloride, becoming cherry-red with bleaching powder. A cherry-red precipitate of the *barium hydroxide* derivative,  $C_{15}H_{10}O_4 \cdot Ba(OH)_2 + H_2O$ , is obtained on adding aqueous barium hydroxide to a dilute solution in alcohol. The *acetyl* derivative crystallises from glacial acetic acid in yellow needles, and melts at 152°; the alcoholic solution develops a brownish-red coloration with ferric chloride, and becomes red when treated with caustic potash. Chrysophanic acid dissolves less readily in ammonia than Liebermann represents; the product of the action of the cold alkali is aminochrysophanic acid.

*Rhabarberone*,  $C_{15}H_{10}O_5$ , crystallises from alcohol in yellow leaflets, and melts at 212°; the alcoholic solution develops a brownish-red coloration with ferric chloride, and an aqueous solution of alkali carbonate dissolves the substance, developing a purple coloration. Hydriodic acid converts it into *rhabarberohydroanthrone*,  $C_{15}H_{12}O_4$ , without eliminating methyl iodide; it crystallises in yellow leaflets and fuses to a black mass at 215–220°.

*Rhein*,  $C_{15}H_{10}O_6$ , melts at 262–265°, and when dissolved in alcohol develops an intense reddish-brown coloration with ferric chloride; acetic anhydride converts it into the *diacetyl* derivative,  $C_{15}H_8O_4(OAc)_2$ .

Austrian rhubarb contains chrysophanic acid, contaminated as usual with methylchrysophanic acid, and *rhapontin*,  $C_{22}H_{24}O_9$ , which crystallises from water in yellowish prisms, and melts, decomposing at 235°. Rhapontin is indifferent towards ferric chloride, and is neutral to litmus, but the aqueous solution becomes acid when boiled; it contains one methoxyl group, dissolves readily in alkalis and alkali carbonates, and forms the *lead* derivative,  $C_{21}H_{20}O_5Pb_2$ . The *tetracetyl* derivative melts at 102°. Rhapontin also occurs in English rhubarb, and the chrysophanic acid derived from this source melts at 188°, and contains only a small proportion of methylchrysophanic acid.

It has been stated by the author (Abstr., 1896, i, 573) that the root of *Rumex nepalensis* yields rumicin, nepalin, and nepodin, of which the first-named had the empirical formula of chrysophanic acid. It now transpires that rumicin is chrysophanic acid, uncontaminated with methylchrysophanic acid, whilst nepalin is identical with nepodin,  $C_{15}H_{10}O_4$ .

The root of *Rumex palustris* contains chrysophanic acid and nepodin, which are also present in *Rumex obtusifolius*, along with *lapodin*,  $C_{15}H_{16}O_5$ , which crystallises from alcohol in yellow needles and melts at 206°, when it decomposes. An alcoholic solution of lapodin develops a dark brown or greenish-brown coloration with ferric chloride, and hydriodic acid does not eliminate a methyl group.

Araroba powder, prepared from a Brazilian wood, is employed in the treatment of skin diseases, and was formerly known as Bahia powder, Goa powder, and chrysarobin. Liebermann and Seidler (*Annalen*, 1882, 212, 29) have employed the last name for indicating a yellow, crystalline compound occurring in Goa powder, and sold in Germany as "chrysophanic acid," although it is quite free from true chrysophanic acid. Owing to the confusion to which this contradiction gives rise, the author has investigated commercial "chrysophanic acid" and araroba powder.

Chrysarobin, obtained by extracting araroba powder with ether,

melts at  $174^{\circ}$ , and has the formula  $C_{15}H_{12}O_3$ , and not  $C_{30}H_{24}O_7$  (compare Liebermann and Seidler); it is usually associated with methylchrysarobin in the proportion 2:1, and for this reason the melting points of different specimens vary widely. Ferric chloride develops a deep brownish-red coloration in the alcoholic solution, and dilute potash dissolves it slowly, forming a yellowish-red solution with feeble green fluorescence; concentrated sulphuric acid also forms a yellowish-red solution, becoming dark brown when warmed. Glacial acetic acid polymerises chrysarobin to *dichrysarobin*, which is readily soluble, and becomes red when treated with dilute potash and exposed to air. Fuming hydrochloric acid at  $100-140^{\circ}$  eliminates a methyl group from methylchrysarobin, and gives rise to chrysophanohydroanthrone, which is isomeric with chrysarobin. Chrysophanohydroanthrone,  $C_{15}H_{12}O_3$ , prepared alike from chrysarobin and chrysophanic acid by the action of hydriodic acid, melts at  $205-210^{\circ}$ , and when mixed with dilute potash and submitted to the action of a current of air, yields chrysophanic acid; the *diacetyl* derivative crystallises from glacial acetic acid in pale yellow needles melting at  $238-240^{\circ}$ , and is indifferent towards ferric chloride.

Chrysarobin yields three acetyl derivatives, which do not produce colour with ferric chloride. The *monoacetyl* derivative, prepared by the action of boiling acetic anhydride, crystallises from glacial acetic acid in yellow leaflets, and melts at  $188-190^{\circ}$ , the solutions in alcohol and acetic acid exhibiting a blue fluorescence. The *diacetyl* derivative, formed when acetic anhydride acts on chrysarobin during 6 hours, crystallises from glacial acetic acid in yellow, rhombic leaflets, and melts at  $216^{\circ}$ ; a pharmaceutical preparation called *lenirobin* appears to consist of this substance mixed with  *$\beta$ -diacetylchrysarobin*, which crystallises from alcohol in yellow needles and melts at  $265-270^{\circ}$ . The *triacetyl* derivative, obtained by heating chrysophanohydroanthrone with acetic anhydride and sodium acetate during 1 hour, melts at  $125^{\circ}$ ; if the treatment is prolonged, *hexacetyldichrysarobin*,  $C_{30}H_{18}(OAc)_6$ , is formed. *Eurobin* is a pharmaceutical preparation composed principally of diacetyldichrysarobin.

The constitution of the foregoing compounds is discussed in the paper.

M. O. F.

**Naphthapurpurin (Trihydroxy- $\alpha$ -naphthaquinone).** By GEORGE F. JAUBERT (*Compt. rend.*, 1899, 129, 684-686).—Naphthazarin, on oxidation with manganese dioxide and sulphuric acid, gives *trihydroxy- $\alpha$ -naphthaquinone*,  $[OH \cdot OH \cdot OH :: 1:2:4]$ , which, from its analogy to purpurin, the author terms *naphthapurpurin*. This forms reddish-brown needles, which can be melted or sublimed, and are sparingly soluble in cold, but very easily in hot water, forming a yellowish-brown solution, which is decolorised by zinc dust with probable formation of pentahydroxynaphthalene. Naphthapurpurin possesses well marked dyeing properties; with an aluminium mordant, cotton is dyed a carmine red, and with a chromium mordant wool is dyed a dull brown. Naphthapurpurin forms acetyl and benzoyl derivatives.

H. R. LE S.

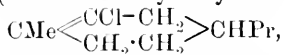
**The Carvone Series.** By AUGUST KIAGES and A. KRAITH (*Ber.*, 1899, 32, 2550-2563).—By converting the members of the carvone



series into 2-chlorocymene it is shown that the ketone group in carvone compounds occupies the ortho-position to the methyl group.

*2-Chlorohexahydrocymene*, obtained by the action of phosphorus pentachloride on tetrahydrocarveol, boils at  $85^\circ$  under 20 mm. pressure, has a sp. gr. 0.935 at  $18^\circ$ , and a refractive index  $n_D$  1.46179.

*2-Chloro- $\Delta^1$ -terpene* (2-chlorotetrahydrocymene),



prepared by the action of phosphorus pentachloride on carvomenthone boils at  $210-211^\circ$  under ordinary pressure, and at  $112^\circ$  under 20 mm. pressure; it has a sp. gr. 1.001 at  $18^\circ$ , and an index of refraction  $n_D$  1.52301. When treated with a molecular proportion of bromine, it yields *2-chlorobromotetrahydrocymene*,  $\text{C}_{10}\text{H}_{16}\text{ClBr}$ , which is an oil having a sp. gr. 1.423 at  $18^\circ$ ; on boiling with quinoline, it loses the elements of hydrogen bromide, *2-chlorodihydrocymene*,  $\text{C}_{10}\text{H}_{15}\text{Cl}$ , being formed as a colourless oil boiling at  $210-212^\circ$ , and having a sp. gr. 1.01 at  $18^\circ$  and a refractive index  $n_D$  1.51202. The action of bromine on this compound gives rise to *2-chlorobromodihydrocymene*,  $\text{C}_{10}\text{H}_{14}\text{ClBr}$ , which is a heavy, brown oil of sp. gr. 1.543 at  $18^\circ$ , and when treated with quinoline yields 2-chlorocymene. The authors find the melting point of 2-chlorocymenesulphonic acid to be  $125^\circ$ , the value formerly obtained by Jünger and Klages being  $135^\circ$ , which is regarded as erroneous.

*Carvone dichloride*,  $\text{CMe} \begin{array}{c} \text{< CCl=CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{> CH} \cdot \text{CMe}_2\text{Cl}$ , is a slightly coloured oil having a sp. gr. 1.188 at  $18^\circ$ ; it is converted into 2-chlorocymene when heated either with quinoline or with dilute sulphuric acid under pressure, or with methyl alcoholic potash. 2-Chlorocymene is obtained directly from carvone by adding the latter to phosphorus pentachloride covered with a layer of light petroleum, and 2-bromocymene is obtained in a similar manner from carvone and phosphorus pentabromide. With carvone and phosphorus triiodide, an oil is obtained which, either when treated with methyl alcoholic potash or when distilled with quinoline, gives rise to a product free from iodine. Eucarvone also yields 2-chlorocymene when treated with phosphorus pentachloride. Owing to the good yields obtained, 2-chloro- and 2-bromo-cymenes may be conveniently prepared by the above method.

*2-Chloro- $\Delta^{1,3}$ -terpadiene*,  $\text{CMe} \begin{array}{c} \text{< CCl-CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{> CPr}^{\beta}$ , obtained from carvenone and phosphorus pentachloride, is a colourless oil which boils under ordinary pressure at  $207-208^\circ$  and under 16 mm. pressure at  $105^\circ$ , has a sp. gr. 1.023 at  $20^\circ$  and a refractive index  $n_D$  1.51620; treatment with sulphuric acid reconverts it into carvenone. The *2-chlorobromoterpadiene*,  $\text{C}_{10}\text{H}_{14}\text{ClBr}$ , on distillation with quinoline, yields 2-chlorocymene.

Dihydrocarvone yields a *chloride*,  $\text{C}_{10}\text{H}_{15}\text{Cl}$ , which boils at  $208^\circ$  under ordinary pressure and at  $105-106^\circ$  under 16 mm. pressure, has a sp. gr. 1.025 at  $18^\circ$  and a refractive index  $n_D$  1.51622; its physical constants point to its identity with the chloride obtained from carvenone.

*Dihydroeucarveol acetate*,  $\text{C}_{12}\text{H}_{20}\text{O}_2$ , boils at  $223-224^\circ$  (corr.), has a

sp. gr. 0.951 at 20°, and a refractive index  $n_D$  1.46315; the isomeric *dihydrocarveol acetate* is a pleasant ethereal-smelling oil which boils at 231–232° and has a sp. gr. 0.947 at 18°. From neither of these acetates is acetic acid removed by boiling with quinoline.

*Dihydroeucarveol chloride*,  $C_{10}H_{17}Cl$ , boils at 85° under 20 mm. pressure; it does not yield 2-chlorocymene, but is converted into Baeyer's euterpene (Abstr., 1898, i, 676).

On treatment with phosphorus pentachloride, dihydroeucarvone yields a *chloride*,  $C_{10}H_{15}Cl$ , boiling at 92–93° under 18 mm. pressure, and having a sp. gr. 1.02 at 18° and a refractive index  $n_D$  1.51250. On treating this chloride with excess of bromine and distilling the compound thus obtained with quinoline, two products were formed, one does not contain chlorine and the other,  $C_{10}H_{15}Cl$ , is isomeric with 2-chlorocymene, but does not yield a sulphonic acid and is oxidised by cold permanganate.

T. H. P.

**Pulegone and Methylhexanone.** By AUGUST KLAGES (*Ber.*, 1899, 32, 2564–2569).—Pulegone in acetic acid solution absorbs bromine, giving a bromide which, when heated, loses hydrogen bromide and yields methylcyclohexanone and *m*-cresol.

3-Chloro- $\Delta^{2(48)}$ -terpadiene,  $CHMe \begin{smallmatrix} \text{CH}=\text{CCl} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} C: CMe_2$ , obtained by the action of phosphorus pentachloride on pulegone, is a colourless oil, boils at 101° under 25 mm. pressure, has a sp. gr. 0.983 at 19°, and a refractive index  $n_D$  1.49928. With excess of bromine, it yields a *tetrabromo*-derivative,  $C_{10}H_{11}ClBr_4$ , as a dark-coloured oil; treatment of this compound with quinoline gives a product having the boiling point of chlorocymene (212–216°), which, however, does not yield a sulphonic acid. Formic acid converts the chloroterpadiene into methylcyclohexanone; a good method of preparing the latter is by the action of formic acid on pulegone.

When methylcyclohexanone is brominated, and the product heated with quinoline, *m*-cresol is obtained.

3:3 *Dichlorohexahydrotoluene*,  $CH_2 \begin{smallmatrix} \text{CCl}_2 - \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} CH_2$ , is formed by the interaction of phosphorus pentachloride and methylcyclohexanone in the cold. If the mixture is not cooled, *m*-chlorotetrahydrotoluene,  $C_7H_{11}Cl$ , is obtained as an oil boiling at 76–79° under 29 mm. pressure and decomposing at 160–170° under ordinary pressure; it has a sp. gr. 1.021 at 18°, and a refractive index  $n_D$  1.48891. On brominating this compound and heating with quinoline, *m*-chlorotoluene is obtained.

T. H. P.

**Terpenes and Ethereal Oils: Ring Disruption and Ring Formation among Terpene Derivatives.** By OTTO WALLACH (*Annalen*, 1899, 309, 1–31).—The oximes of cyclic ketones usually undergo ring disruption with great facility, yielding the nitrile of an unsaturated aliphatic acid, with an isoxime as intermediate compound; cyclic bases frequently occur as bye-products. Conversely, aliphatic unsaturated ketones may be converted into cyclic bases by reducing the oxime, adding bromine to the amine thus obtained, and withdrawing 2HBr from the product.

[With TH. BÖCKER].—A mixture of concentrated sulphuric and glacial acetic acids converts methylhexanoneoxime into the  $\alpha$ -isoxime,  $C_7H_{13}ON$ , melting at  $104-105^\circ$ , which has  $\alpha_D -3.2^\circ$  in alcohol, and the  $\beta$ -isoxime, which melts at  $65-66^\circ$ ; these compounds are distinguished from the original oxime by their solubility in water, and also by their stability towards dilute acids, which do not affect them even when boiled. The isoximes are feeble bases, and form readily soluble hydrochlorides, and compounds with alkyl iodides; their constitution is most likely expressed by the formulæ  $CH_2<\begin{smallmatrix} CHMe-CH_2 \\ CH_2\cdot CH_2\cdot CO \end{smallmatrix}>NH$  and  $CH_2<\begin{smallmatrix} CHMe-CH_2 \\ CH_2\cdot CH_2\cdot NH \end{smallmatrix}>CO$ , but the possibility of physical isomerism is not excluded, as both forms boil at  $154-155^\circ$  under 14 mm. pressure, and at  $278-279^\circ$  under atmospheric pressure.

Phosphoric oxide acts vigorously on methylhexanoneoxime, producing unsaturated hydrocarbons of the aliphatic series, together with toluene, dihydrotoluene, and the nitrile of an unsaturated acid,  $C_7H_{12}O_2$ , probably identical with Fittig's  $\beta\gamma$ -isoheptenoic acid. This acid boils at  $120-121^\circ$  under 12 mm. pressure, at  $219-222^\circ$  under atmospheric pressure, and has a molecular refraction  $35.92$ ; the amide melts at  $68-70^\circ$ , the calcium salt contains  $1\frac{1}{2}H_2O$ , and the isomeric lactone is a liquid which boils at  $116-120^\circ$  under reduced pressure.

[With W. RATH].—Methylhexanoneoxime and phosphoric oxide also give rise to a lutidine,  $C_7H_9N$ , which shows some resemblance to 2:6-dimethylpyridine. It boils at  $148-156^\circ$ , forms a picrate which melts at  $163-164^\circ$ , and a platinichloride which crystallises from alcoholic hydrochloric acid in thick plates and melts at  $197-198^\circ$ ; the aurichloride melts at  $127-128^\circ$ .

Phosphoric oxide converts methylpentanoneoxime into volatile hydrocarbons, the nitrile of  $\beta\gamma$ -hexenoic acid and 3-methylpyridine.

A mixture of glacial acetic and concentrated sulphuric acids transforms suberoneoxime into the isoxime,  $C_7H_{13}ON$ , which melts at  $25^\circ$  and boils at  $156^\circ$  under 8 mm. pressure; the hydrochloride dissolves very readily in water, and the platinichloride forms large crystals. Phosphoric oxide acts on the isoxime when heated, forming the nitrile of a heptenoic acid,  $C_7H_{12}O_2$ .

Thujaketoneoxime,  $C_9H_{16}NOH$ , derived from methyl heptylene ketone (Abstr., 1893, i, 107), boils at  $118-120^\circ$  under 15 mm. pressure. Reduction converts it into the base,  $C_9H_{17}\cdot NH_2$ , which boils at  $78-79^\circ$  under 26 mm. pressure, and forms the carbamide melting at  $104-105^\circ$ . A base belonging to the pyridine series results on eliminating water from the oxime by means of concentrated sulphuric acid.

[With EUGEN VON BIRON].—Phosphoric oxide acts vigorously on thujaketoneoxime, yielding the base,  $C_9H_{17}N$ , which boils at  $180-183^\circ$ , and has a sp. gr. 0.892 at  $25^\circ$ ; the picrate decomposes above  $170^\circ$  without melting, and the platinichloride melts and decomposes at  $179^\circ$ .

[With HERM. UMBROVE].—The base,  $C_8H_{15}\cdot NH_2$ , obtained by reducing methylheptenoneoxime in alcohol with sodium, boils at  $166-167^\circ$ , has a sp. gr. 0.7975 at  $20^\circ$ , and a molecular refraction 42.47; the picrate, osalate, and carbamide melt at  $112$ ,  $203^\circ$ , and

118° respectively. The *hydrochloride* is hygroscopic, and yields the *platinichloride*, which melts at 165°; the *dihydrochloride* of the base,  $C_8H_{15}Cl \cdot NH_2$ , produced on passing hydrogen chloride into an ethereal solution of the base,  $C_8H_{15} \cdot NH_2$ , melts at 150°.

When bromine (1 mol.) is added to an aqueous solution of the hydrochloride,  $C_8H_{15} \cdot NH_2 \cdot HCl$ , the colour is destroyed, and on evaporating the solution, hydrogen bromide is evolved; caustic soda liberates from the residue the *base*,  $C_8H_{15}N$ , which boils at 145—147°, has a sp. gr. 0.838 at 20°, and a molecular refraction 39.39. The *picrate* and *oxalate* melt at 139° and 141° respectively. The constitution

of the base is expressed by one of the formulæ  $CH_2 \begin{matrix} \swarrow CH_2 - C : CMe_2 \\ \searrow CHMe \cdot NH \end{matrix}$

and  $CH_2 \begin{matrix} \swarrow CH_2 \cdot CH : CMe_2 \\ \searrow CHMe - NH \end{matrix}$ .

[With AD. GILBERT.]—Phosphoric oxide converts methylheptenone-oxime into a *base*,  $C_8H_{13}N$ , which boils at 183°; the *picrate* melts and decomposes at 149—150°, the *platinichloride* decomposes before fusion, and the *aurichloride* forms yellow needles which melt and decompose at 164—165°.

M. O. F.

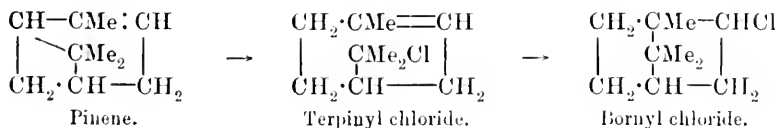
**Relation of Pinene Hydrochloride and Hydriodide to Bornyl Chloride and Iodide.** By GEORG WAGNER and W. BRICKNER (*Ber.*, 1899, 32, 2302—2325).—The authors support the conclusion of Jünger and Klages (*Abstr.*, 1896, i, 313), and of Reychler (*ibid.*), that the isobornyl chloride prepared by the action of phosphorus pentachloride on isoborneol is identical with camphene hydrochloride. They further seek to show that pinene hydrochloride is the true chloride from borneol. The so-called "bornyl chloride," prepared by the action of phosphorus pentachloride on borneol from bornyl acetate, was found to be, for the most part, readily convertible into camphene by boiling with alcoholic potash, and therefore probably consists chiefly of isobornyl chloride (camphene hydrochloride), the borneol being converted first into camphene and then combining with a mol. of hydrogen chloride; a part of the product, however, is much more resistant to the action of alcoholic potash or of water, and it is suggested that this is probably identical with the pinene hydrochloride from turpentine oil. Riban's chloride (*Ann. Chim. Phys.*, 1875, [v], 6, 380—383), prepared by the action of hydrogen chloride on borneol, is regarded as a mixture similar to that produced by the action of phosphorus pentachloride, but containing a larger percentage of true bornyl chloride. Attempts were also made to convert pinene hydrochloride into bornyl acetate by heating it with silver acetate and acetic acid on a water-bath during two days; the product consisted chiefly of camphene and isobornyl acetate, but did not appear to contain any bornyl acetate. The reaction proceeds much more smoothly than that employed by Marsh and Stockdale (*Trans.*, 1890, 57, 963), but it is probable that in each case the isobornyl acetate is produced by addition of acetic acid to camphene (Reychler, *Abstr.*, 1896, i, 313), and not by the direct displacement of the chlorine of the chloride by the acetoxy-radicle.

More definite results were obtained with the iodides. Pinene hydriodide (Deville, *Annalen*, 1841, 37, 176; Baeyer, *Abstr.*, 1893, i, 360)

is best prepared by the action of dry hydrogen iodide on French turpentine oil; it is a stable, heavy, colourless oil which boils at  $118-119^\circ$  under 15 mm. pressure, solidifies in a freezing mixture, melts at  $-3^\circ$ , and has the sp. gr. 1.4826 at  $0^\circ/0^\circ$  and 1.4635 at  $20^\circ/0^\circ$ . When prepared from a turpentine oil of  $[\alpha]_D^{25} 37^\circ 50'$  and washed with aqueous caustic potash, it gave  $\alpha_D -33^\circ 34'$  in a decimetre tube, but on heating with alcoholic potash  $\alpha_D$  became  $-32^\circ 40'$  after 10 hours, and  $-31^\circ 25'$  after 40 hours treatment. It is completely freed from iodine by heating with alcoholic potash at  $160-170^\circ$  for a short time, and at this temperature camphene is the sole product. The iodide is only slowly attacked by potassium permanganate, even on heating, but is oxidised by fuming nitric acid at  $-20^\circ$  with separation of iodine. Silver acetate and acetic acid yield, not only camphene and the two bornyl acetates, but also dipentene and inactive terpinyl acetate; the authors regard dipentene and terpinyl acetate as the normal products of the action, and camphene and isobornyl acetate, which are produced in larger quantities at higher temperatures, are supposed to be formed by a secondary reaction.

Bornyl iodide, when prepared by moistening borneol with a little water and saturating with hydrogen iodide at the temperature of a water-bath, seems to be a mixture of two substances, one of which is readily attacked by alcoholic potash, giving an oily hydrocarbon, whilst the other is only slowly attacked and gives camphene. True *bornyl iodide*, when purified by boiling with an excess of alcoholic potash during 30 hours, closely resembles pinene hydriodide in most of its properties and reactions, but is almost inactive ( $\alpha_D = 1^\circ 30'$  in a decimetre tube); it boils at  $118-119^\circ$  under 16 mm. pressure, has the sp. gr. 1.4799 at  $0^\circ/0^\circ$  and 1.4617 at  $20^\circ/0^\circ$ , solidifies in a freezing mixture, and melts at  $-13^\circ$ ; when treated with silver nitrate and acetic acid, it gives camphene, bornyl acetates, dipentene, and terpinyl acetate; the authors therefore regard it as identical with pinene hydriodide in all respects except its rotatory power. Isoborneol gives an oily *hydriodide* which is decomposed completely by cold alcoholic potash into camphene and potassium iodide.

The formation of bornyl chloride (pinene hydrochloride) from pinene by the action of hydrogen chloride is explained by the use of the formulæ:



The formation of terpinyl chloride by the action of hydrogen chloride has not been definitely proved, although the presence of a strongly active liquid hydrochloride has been repeatedly noticed; its production would, however, be quite analogous to that of terpinyl salts by the action of organic acids on pinene (Reychler, Abstr., 1896, i, 313).

T. M. L.

**Ethereal Oil of Jasmine Flower.** By ALBERT HESSE (*Ber.*, 1899, 32, 2611—2620. Compare Abstr., 1899, i, 376 and 411).—Crude oil of jasmine is warmed with 10 per cent. of picric acid until a clear solution is obtained; on cooling, a considerable quantity of indole picrate separates, and the precipitation is completed by the addition of light petroleum. The amount of indole in the oil is about  $2\frac{1}{2}$  per cent. The *bisulphite* compound of indole is readily produced by shaking together an ethereal solution of indole and a dilute alcoholic solution of sodium hydrogen sulphite; it separates in white, silky leaflets readily soluble in water and sparingly in methylic alcohol. Oil of jasmine also contains a small amount (about  $\frac{1}{2}$  per cent.) of methyl anthranilate; this ester is detected by Erdmann and Walbaum's method (Abstr., 1899, i, 620 and 621). Oil of neroli contains over 1 per cent. of this compound, and in this case it can be separated by adding the oil to a mixture of ether and concentrated sulphuric acid, when the sulphate of methyl anthranilate crystallises out; under these conditions, no precipitate is obtained with oil of jasmine.

Oil of jasmine is treated with picric acid and petroleum to remove indole, and then fractionated under diminished pressure; the fraction distilling at  $100^{\circ}$  under a pressure of 4 mm. is heated with hydroxylamine hydrochloride and alcoholic potash. The crude oxime is purified either by distilling with steam or by reprecipitation with ammonia from its solution in dilute sulphuric acid.

*Jasmone*,  $C_{11}H_{16}O$ , is obtained by hydrolysing the oxime with hot dilute sulphuric acid; the new ketone boils at  $257$ — $258^{\circ}$  under a pressure of 755 mm., and has a sp. gr. 0.945 at  $15^{\circ}$ . *Jasmone oxime*,  $C_{11}H_{17}ON$ , crystallises from dilute alcohol in needles, and melts at  $45^{\circ}$ . *Jasmone semicarbazone* melts at  $200$ — $204^{\circ}$ ; it is probably a mixture because crystallisation from alcohol separates it into a less soluble substance melting at  $204$ — $206$ , and a more soluble melting at  $199$ — $201^{\circ}$ . The constituents of the oil of jasmine are:

Jasmone .....	3.0 per cent.	Linalyl acetate.....	7.5 per cent.
Indole .....	2.5 „	Benzyl alcohol .....	6.0 „
Methyl anthranilate ..	0.5 „	Linalool .....	15.5 „
Benzyl acetate .....	65.0 „		
			100.0
			G. T. M.

**Natural Resins [Ueberwallungsharze]. V.** By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1899, 20, 755—761. Compare Abstr., 1899, i, 929).—The isolariciresinol, which was obtained (*loc. cit.*) by the hydrolysis of the acetyl derivatives of larciresinol, is also formed when larciresinol is treated with sodium in amyl alcoholic solution; it crystallises in laminae from dilute alcohol, and melts at  $95$ — $97^{\circ}$ . The *tetracetyl* derivative melts at  $160^{\circ}$ . The *dimethoxy*-derivative crystallises from alcohol in long needles melting at  $165^{\circ}$ , but the diethoxy-derivative is apparently identical with diethoxylarciresinol. If this isolariciresinol is boiled in benzene solution, it is transformed into an isomeric substance,  $C_{19}H_{22}O_6$ , which melts at  $152$ — $153^{\circ}$ .

and on recrystallisation from alcohol is reconverted to isolariciresinol being probably a physical isomeride of this latter substance.

R. H. P.

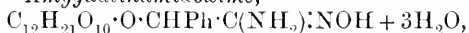
**Ethereal Oils of Cresses, and the Glucosides from which they are formed.** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 507—521).—The method adopted was that found suitable in the case of *Tropaeolum majus* (compare Abstr., 1899, i, 535).

From *Lepidium sativum* (garden cress) the same products were obtained as from *Tropaeolum*, namely, benzylthiocarbimide and silver tropeolate.

From *Nasturtium officinale* (watercress), phenylethylthiocarbimide,  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{NCS}$ , is obtained. The glucoside, *gluconasturtiin*, is a different one; on treatment with silver nitrate, it yields *silver nasturtiate*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}(\text{SAg})\cdot\text{O}\cdot\text{SO}_2\cdot\text{OAg} + 2\text{H}_2\text{O}$ , which is soluble in ammonia in the presence of ammonium nitrate, but is precipitated by nitric acid, and is decomposed by sodium thiosulphate into phenylethylthiocarbimide and sodium sulphate. When an attempt was made to prepare an additive compound of the silver salt with ammonia, it was found that some of the silver was replaced at the same time by ammonium. It is noteworthy that the seeds do not contain an appreciable quantity of any enzyme capable of hydrolysing the glucoside.

*Barbarea precox* (American cress) yields the same products as *Nasturtium*.  
C. F. B.

**Amygdalinamidoxime.** By HUGO SCHIFF (*Ber.*, 1899, 32, 2699—2702).—*Amygdalinamidoxime*,



is prepared by the action of hydroxylamine on amygdalin; it crystallises from dilute alcohol, decomposes at about  $160^\circ$ , has only a slightly bitter taste, and dissolves readily in water, but not in absolute alcohol, benzene or chloroform. It is levorotatory,  $[\alpha]_D - 72.2^\circ$ ; the mol. weight, determined from the freezing point of a solution in phenol, was 462 (calc. 490).

T. M. L.

**Extractum Filicis Aethereum.** By ARTHUR HAUSMANN (*Arch. Pharm.*, 1899, 237, 544—560. Compare Boehm, Abstr., 1898, i, 40).—Aspidin does not occur in extracts prepared from the roots of *Aspidium Filix mas*, Sw.; it is found in *Aspidium spinulosum*, Sw., however, and, when detected in a commercial extract, owes its presence probably to the fact that a comparatively inexpert collector has mistaken, as can easily be done, the roots of *A. spinulosum* for those of *A. Filix mas*, which are prescribed officinally. Filicic acid is present in extracts both from *A. Filix mas* and *Athyrium Filix femina*, Roth. Flavaspidic acid occurs in the extracts from all the ferns enumerated above. Albaspidin and aspidinol occur in extracts containing filicic acid, as well as in those which contain aspidin.

Poulsen's (Abstr., 1896, i, 387; 1899, i, 379) yellow and white polystichinic acids (polystichin and polystichalbin) are possibly identical with aspidin and albaspidin, and either his polystichocitrin or polystichoflavin with flavaspidic acid; in no case, however, do the analyses agree.

C. F. B.

**Constitution of the Colouring Matter of Leaves: Chloroglobulin.** By TSVETT (*Compt. rend.*, 1899, 129, 607—610).—When plant leaves are treated with a concentrated aqueous solution of resorcinol made slightly alkaline with ammonium carbonate, the chloroplasts swell up and agglomerate, and various constituents of the cells are dissolved or liquefied, whilst the colouring matter collects in large, oily-looking drops, which coagulate at once if the resorcinol is washed out by glycerol or water. These green globules, which the author calls *chloroglobin*, are insoluble in saline solutions, but swell up in some of them (dipotassium hydrogen phosphate and potassium carbonate), and are altered by potassium carbonate; they are slowly decomposed by dilute acids, and are completely dissolved and decomposed by concentrated acids. Like many proteids, the globules absorb and retain colouring matters such as magenta, cyanin, chrysoidin, methylene-blue, and iodine-green. Chloroglobulin swells up in solutions of alkali hypochlorites and is decolorised; the bleached substance gives indefinite results with the ordinary reagents for proteids. It dissolves in strong alcohol, and if this solution is agitated with benzene, a green colouring matter, which is not affected by resorcinol, passes into the latter, and a yellow substance, which is liquefied by resorcinol, remains in the alcohol.

In physico-chemical properties, chloroglobulin resembles the proteids; the solubility in ether, carbon disulphide, and other organic solvents, seems to be due to the chromophoric nucleus in the molecule. The chlorophyll and carotin (xanthophyll) are probably loosely associated with the proteid nucleus.

Chloroglobulin can be obtained in a very pure condition by extracting suitable leaves with strong alcohol, diluting to 20°, and collecting the very fine precipitate by filtration through porcelain. C. H. B.

**Alkaloids of the Solanaceæ.** By OSWALD HESSE (*Annalen*, 1899, 309, 75—94. Compare Abstr., 1892, 1498).—A specimen of atropine has been obtained from the root of *Scopolia atropoides* entirely devoid of optical activity; it melts at 115·5—116°, and the hydrobromide and hydrochloride, which are also inactive, melt at 162° and 165° respectively. The aurichloride and oxalate melt at 136° and 190—191° respectively. Gadamer (Abstr., 1897, i, 132) has also prepared inactive atropine, attributing the activity of the commercial alkaloid to the presence of hyoscyamine, and this has been found by the author to be the explanation. The rotatory power diminishes when the alkaloid is kept in the free condition, but the activity of the sulphate undergoes no change. Atropine aurichloride, contaminated with hyoscyamine aurichloride, becomes transformed into the latter in two years; the individual salt, however, undergoes no change.

The rotatory power of hyoscyamine also changes when the free alkaloid is kept, but the sulphate does not alter.

Atroscine, obtained from commercial scopalamine hydrobromide (Abstr., 1896, i, 655), melts at 82—83° when anhydrous, and is optically inactive; it crystallises with 1H<sub>2</sub>O, then melting at 56—57°, and with 2H<sub>2</sub>O, when it melts at 36—37°. The hydrobromide crystallises with  $\frac{1}{2}$ H<sub>2</sub>O and with 3H<sub>2</sub>O, and melts at 181° when anhydrous. One specimen of commercial scopalamine hydrobromide examined by the



author contained 15 per cent. of atrosine hydrobromide, but all others contained 44·8—83·7 per cent. ; the new, crystallised alkaloid, obtained by E. Schmidt from hyoscyne, is stated by the author to be impure atrosine, and this is also true of Luboldt's scopolamine (Abstr., 1898, i, 499).

The author emphasises the opinion already expressed (Abstr., 1897, i, 132) that the name scopolamine is misleading, as the commercial hydrobromide is a mixture of hyoscyne and atrosine hydrobromides.

M. O. F.

**Narcotine.** By WILHELM ROSER (*Ber.*, 1899, 32, 2974. Compare *Annalen*, 1888, 247, 168).—The author points out that Frankforter and Keller (Abstr., 1899, i, 781) are in error in attributing to him the statement that dimethyltolueneazammonium silver iodide is formed by the action of silver chloride on narcotine methiodide.

A. H.

**$\alpha$ -Dinitrophenylpyridine Chloride.** By EDUARD VONGERICHTEN (*Ber.*, 1899, 32, 2571—2572).—One-tenth of a per cent. of pyridine in aqueous or alcoholic solution may be detected as follows. An alcoholic solution of  $\alpha$ -chlorodinitrobenzene is added to the liquid, and the mixture then gently warmed and shaken; after cooling, the addition of sodium hydroxide solution produces a reddish-violet colour if pyridine is present.

A solution of  $\alpha$ -chlorodinitrobenzene in excess of pyridine gradually deposits an additive compound,  $C_{11}H_8O_4N_3Cl$ , which crystallises from methyl alcohol in long, flat prisms and from acetic acid in groups of radiating needles; it is very soluble in water or alcohol, and gives a white precipitate with silver nitrate; the *platinichloride*,  $(C_{11}H_8O_4N_3)_2PtCl_6$ , and *aureichloride*,  $C_{11}H_8O_4N_3AuCl_4$ , form yellow precipitates. Freshly precipitated silver oxide produces in the aqueous solution no alkaline reaction, but a red, crystalline precipitate soluble in sodium hydroxide solution with the formation of a reddish-violet coloration. The addition of sodium carbonate gives a thick brown precipitate, gradually changing into a heavy, scarlet, crystalline deposit, which also gives a reddish-violet colour when dissolved in sodium hydroxide; the same coloration is obtained by the direct addition of sodium hydroxide solution to the aqueous chloride. The red, crystalline compound has the composition  $(C_{11}H_8O_4N_3)_2O$ , and is the *anhydride* of the ammonium base corresponding with the chloride.

T. H. P.

**Dinitrophenylpyridine Chloride.** By LEOPOLD SPIEGEL (*Ber.*, 1899, 32, 2834—2836. Compare Vongerichten, preceding abstract, and Gail, *Diss. Marburg*, 1899).—The aureichloride of dinitrophenylpyridine chloride crystallises from hot water in golden flakes. The product of the action of alkalis on the chloride has the composition of an ammonium base (Gail), and not of an anhydride (Vongerichten). The chloride is oxidised by potassium permanganate and by chromic acid to dinitraniline, showing that the phenyl group is linked to the nitrogen, and not to the carbon, of the pyridine ring.

T. M. L.

**Alkyl Salts of Quinolinic and Cinchomeronic Acids.** By ALFRED KIRPAL (*Monatsh.*, 1899, 20, 766—778).— $\beta$ -Methyl quinolinate

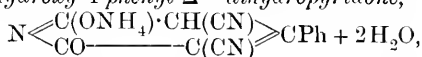
is obtained when quinolinic anhydride is boiled for 4 hours with methyl alcohol and a little acetic anhydride; it forms colourless, rhombohedral crystals from ethyl acetate melting at  $123^{\circ}$ , and its metallic salts are very similar to those of picolinic acid. When heated above its melting point, carbon dioxide is eliminated with the formation of methyl nicotinate. The corresponding  $\beta$ -ethyl quinolinate crystallises from benzene in colourless leaflets melting at  $132^{\circ}$ .

Monomethyl cinchomerate, first prepared by Goldschmiedt and Strache (Abstr., 1889, 1016), melts at  $172^{\circ}$ . Its metallic salts are very similar to those of nicotinic acid, and it is probably therefore the  $\gamma$ -methyl cinchomerate. Dimethyl cinchomerate is a yellow oil which cannot be distilled. The hydrochloride melts at  $141^{\circ}$ . The author was not successful in obtaining the  $\alpha$ -alkyl quinolates or  $\beta$ -alkyl cinchomerates.

These compounds were prepared in order to test Wegscheider's rule for the esterification of dibasic acids (Abstr., 1895, ii, 310) and the results taken in conjunction with those of Goldschmiedt and Kirpal on the esterification of papaverinic acid (Abstr., 1897, i, 131) lead to the conclusion that the rule is not applicable to pyridinedicarboxylic acids.

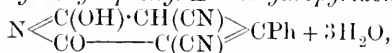
R. H. P.

**Dicyanohydroxypyridones.** By ICILIO GUARESCHI (*Chem. Centr.*, 1899, ii, 118—120; from *Atti Real. Accad. Torino*, 34. Compare Abstr., 1898, i, 274).—By the action of ammonia solution of sp. gr. 0.914 on a mixture of benzaldehyde (about 1 mol.), ethyl methylcyanoacetate and ethyl ethylcyanoacetate, the ammonium derivative of 3:5-dicyano-6-hydroxy-4-phenyl- $\Delta^{3,6}$ -dihydropyridone,



is obtained, together with a substance, melting at  $169^{\circ}$ , identical with Carrick's compound,  $\text{CHPh}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ ,  $\text{CHPh}:\text{C}(\text{CN})\cdot\text{CONH}_2$ , (Abstr., 1892, 1086). Carrick gives the melting point as  $168^{\circ}$ , and probably also obtained a mixture of this compound with the ammonium derivative of the dicyanohydroxyphenyldihydropyridone. This ammonium derivative is also obtained by the action of ammonia gas on a mixture of benzaldehyde and ethyl cyanoacetate; it crystallises from hot water in lustrous, colourless needles, is insoluble in hydrochloric acid, decomposes when heated with liberation of ammonia, forms silver, calcium, barium, &c., salts, gives a characteristic precipitate with nicotine hydrochloride, but not with coniine hydrochloride.

3:5-Dicyano-6-hydroxy-4-phenyl- $\Delta^{3,6}$ -dihydropyridone,



or dicyanophenylglutaconimide, obtained from the ammonium derivative by precipitating the silver salt and then decomposing it with hydrogen sulphide, crystallises from water in colourless needles and melts at  $234$ — $235^{\circ}$ . When dissolved in water, it forms a strongly acid solution. The silver, barium, magnesium, iron, copper, and copper-ammonium derivatives are described.

3:5-Dicyano-6-hydroxy-4-p-methoxyphenyl- $\Delta^{3,6}$ -dihydropyridone,



prepared by the action of ammonia on anisaldehyde and ethyl cyanoacetate, forms colourless crystals which are soluble in water and become coloured on exposure to the air. The corresponding *ammonium* derivative crystallises in colourless, monohydrated needles. The silver, iron, and copper-ammonium derivatives are described. A compound similar to Carrick's salt is also formed by the action of ammonia on anisaldehyde and ethyl cyanoacetate; it is only very slightly soluble in boiling water and melts at 166°.

By the action of ammonia on furfuraldehyde and ethyl cyanoacetate, the *ammonium* derivative of 3:5-dicyano-6-hydroxy-4-furfuryl- $\Delta^{3,6}$ -dihydropyridone,  $\text{NH}_4 \cdot \text{C}_{11}\text{H}_4\text{O}_3\text{N}_3$ , is obtained, but apparently without the formation of any bye-product; it crystallises in long, colourless, silky needles, is very soluble in boiling water, and dissolves in 550 parts of cold water.

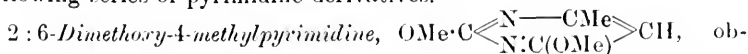
3:5-Dicyano-6-hydroxy-4-furfuryl- $\Delta^{3,6}$ -dihydropyridone,



crystallises in long, silky needles and is soluble in warm water; the anhydrous compound melts and decomposes at 260—265°. The barium, magnesium, copper, and copper-ammonium derivatives are described. *Ethyl furfuryl- $\alpha$ -cyanoacrylate*,  $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , prepared by the action of a 1—2 per cent. solution of methylamine on furfuraldehyde and ethyl cyanoacetate, melts at 93—94°. Citral also reacts with ethyl cyanoacetate in presence of ammonia. E. W. W.

**Benzoylpyridinecarboxylic Acids.** By HUGO L. FULDA (*Monatsh.*, 1899, 20, 762—765).—The author has repeated Freund's experiments (Abstr., 1898, i, 43), which were not in accordance with those of Jeiteles (Abstr., 1897, i, 97), on the condensation of cinchononic anhydride and benzene. He finds that carbon dioxide is eliminated from the condensation product at 260°. The resulting ketone distils at 300°, melts at 63—65° and forms an oxime melting at 163—164°. The condensation product, on oxidation with acidified potassium permanganate, yields isonicotinic acid, and therefore must be 4-benzoyl-nicotinic acid. R. H. P.

**Derivatives of 4-Methylpyrimidine [4-Methyl-*m*-diazine].** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1899, 32, 2921—2935. Compare Abstr., 1899, i, 638).—The chlorine atoms of 2:6-dichloro-4-methylpyrimidine may be replaced by hydrogen, and also by other elementary and compound radicles; this substitution gives rise to the following series of pyrimidine derivatives.



tained by heating the dichloro-base with sodium methoxide and methyl alcohol, melts at 69—70°, and boils at 213° under a pressure of 763 mm.; it is a strong base, its platinichloride and aurichloride crystallise in orange-yellow and lemon-yellow needles respectively, and its picrate forms sparingly soluble, yellow leaflets.

4-Methylpyrimidine-2 : 6-dithiol,  $\text{HS} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{CMe} \\ \text{N} : \text{C}(\text{SH}) \end{smallmatrix} \text{CH}$ , prepared by heating the dichloro-base with alcoholic potassium hydrosulphide, separates in rhombic needles when acetic acid is added to its solution in potassium hydroxide; it is almost insoluble in water and the ordinary organic solvents, and does not melt below  $280^\circ$ .

When the dichloro-base is treated with alcoholic ammonia, one or other of the chlorine atoms is replaced by amidogen; the separation of the two isomerides depends on their different solubilities in alcohol.

6-Chloro-2-amino-4-methylpyrimidine,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} = \text{CCl} \end{smallmatrix} \text{CH}$ , the more soluble isomeride, crystallises in colourless needles melting at  $181-182^\circ$ ; its platinichloride, aurichloride, chromate, picrate, and ferrocyanide form a well-defined series of sparingly soluble salts; the base is also obtained by heating iminomethyluracil,

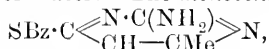


with phosphorus oxychloride, and this mode of formation serves to determine the constitution of the compound. When the base is heated with hydriodic acid and red phosphorus, iminomethyluracil is regenerated.

2-Amino-4-methylpyrimidine,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} = \text{CH} \end{smallmatrix} \text{CH}$ , produced by reducing 6-chloro-2-amino-4-methylpyrimidine with zinc dust and water, crystallises from water in glistening leaflets, and sublimes in silky needles; it melts at  $159-160^\circ$ , and has an odour resembling that of acetamide.

2-Amino-6-anilino-4-methylpyrimidine,  $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{CH} = \text{CMe} \\ \text{N} \cdot \text{C}(\text{NH}_2) \end{smallmatrix} \text{N}$ , prepared by heating 6-chloro-2-amino-4-methylpyrimidine with aniline, crystallises from its hot aqueous or alcoholic solution in needles melting at  $173^\circ$ ; the platinichloride, aurichloride, chromate, and picrate are obtained as yellow, crystalline salts.

2-Amino-4-methylpyrimidine-6-thiol,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} - \text{CMe} \\ \text{N} : \text{C}(\text{SH}) \end{smallmatrix} \text{CH}$ , obtained by heating the corresponding chloropyrimidine with alcoholic potassium hydrosulphide at  $100^\circ$ , crystallises in yellow needles which are readily soluble in caustic alkalis or hydrochloric acid, but only sparingly so in alcohol or water. The monobenzoyl derivative,



crystallises from dilute alcohol in obliquely truncated needles, and is insoluble in alkaline solutions; it sinters at  $128^\circ$  and melts at  $130-133^\circ$ ; when heated for some time above its melting point, it changes into an isomeride, which crystallises in yellow rhombohedra and melts at  $189^\circ$ ; this substance dissolves in solutions of caustic alkalis, and probably results from the migration of the benzoyl group from the sulphur atom to the aminic nitrogen.

2-Chloro-6-amino-4-methylpyrimidine,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} - \text{CCl} \\ \text{CH} : \text{CMe} \end{smallmatrix} \text{N}$ , the

less soluble isomeride, crystallises in colourless, truncated prisms, and melts at 215—216°; the platinichloride, aurichloride, chromate, and picrate are well-defined, yellow salts.

6-Amino-4-methylpyrimidine,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CH} \\ \text{CH} : \text{CMe} \end{smallmatrix} \text{N}$ , prepared by reducing the preceding compound either with hydriodic acid and red phosphorus or zinc dust and water, crystallises in lustrous prisms melting at 194—195°; the aqueous solution of the base has a strongly alkaline reaction, whereas that of its 4 : 2 : 6-isomeride is neutral, the platinichloride, aurichloride, and picrate are well-defined crystalline compounds.

6-Amino-2-anilino-4-methylpyrimidine,  $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CMe} \\ \text{N} : \text{C}(\text{NH}_2) \end{smallmatrix} \text{CH}$ , crystallises from dilute alcohol in lustrous leaflets and melts at 118—119°.

6-Amino-4-methylpyrimidine-2-thiol,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH} : \text{CMe} \\ \text{N} \cdot \text{C}(\text{SH}) \end{smallmatrix} \text{N}$ , crystallises from hot water in iridescent, rhombic plates or flattened needles which darken on heating, but do not melt below 280°.

The hydriodide of 6-hydroxy-4-methylpyrimidine is prepared by heating 2 : 6-dichloro-4-methylpyrimidine with hydriodic acid (b. p. 127°) and red phosphorus; the base is obtained by shaking a solution of this salt with moist silver oxide; it crystallises from benzene in colourless needles melting at 149—150°.

6-Chloro-4-methylpyrimidine,  $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} = \text{CCl} \end{smallmatrix} \text{CH}$ , produced by heating the preceding base with phosphorus oxychloride on the water-bath, melts at 38—39·5°, and boils at 173—174° under a pressure of 758 mm.; its odour resembles that of nitrobenzyl chloride. That this compound has the constitution indicated by the formula is shown by the fact that it yields 6-amino-4-methylpyrimidine when heated at 100° with alcoholic ammonia.

6-Anilino-4-methylpyrimidine,  $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CH} \\ \text{CH} : \text{CMe} \end{smallmatrix} \text{N}$ , obtained by heating aniline and the preceding chloro-base at 100°, crystallises from water in felted needles melting at 146°; its platinichloride forms felted, yellow needles.

4-Methylpyrimidine-6-thiol, prepared by heating 6-chloro-4-methylpyrimidine with an alcoholic solution of potassium hydrosulphide, crystallises from boiling water in obliquely truncated needles or rhombic plates; it melts and decomposes at 255°, and is readily soluble in caustic alkalis.

The disulphide,  $(\text{C}_5\text{H}_5\text{N}_2)_2\text{S}_2$ , formed by oxidising the sodium derivative of the preceding thiol-base with a solution of iodine in potassium iodide, separates from light petroleum in granular crystals melting at 105—107°.

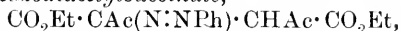
6-Iodo-4-methylpyrimidine,  $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} = \text{CI} \end{smallmatrix} \text{CH}$ , is obtained as hydriodide by the action of fuming hydriodic acid on 2 : 6-dichloro-4-methylpyrimidine (*loc. cit.*), melts at 20°, and yields 6-anilino-4-methylpyrimidine on heating at 100° with aniline. When the

2:6:4- or the 6:2:4-chloroaminomethylpyrimidine is heated at 195° with carbamide, a *compound* is obtained having a composition corresponding with that required by the formula  $C_8H_{11}O_3N_7$ .

The *base*,  $C_{10}H_6O_2N_6$ , produced by adding 4-methylpyrimidine to excess of fuming nitric acid, crystallises from water in glistening rhombohedra or rhombic plates, and melts at 134°; the *nitrate* crystallises in thick, yellow prisms melting at 157°; and the *platinichloride* forms orange-yellow needles.  
G. T. M.

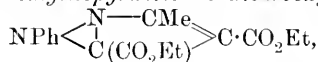
**Preparation of Isopyrazole Derivatives from Diethyl Benzeneazodiacetylsuccinate.** By CARL BÜLOW and ALFRED SCHLESINGER (*Ber.*, 1899, 32, 2880—2891).—The elimination of an acetyl group from  $\alpha$ -substituted ethyl acetoacetates,  $CHRAc \cdot CO_2Et$ , is a necessary step in the formation of hydrazones,  $N_2HPh \cdot CR \cdot CO_2Et$ , by the action of diazo- and isodiazo-compounds on these esters (V. Meyer, *Abstr.*, 1888, 366) and the results of previous investigators indicate that the reaction invariably takes place in this sense (Japp and Klingemann, *Trans.*, 1888, 53, 332, and Bischler, *Abstr.*, 1893, i, 44 and 610). Benzenediazonium chloride, however, combines with diethyl diacetylsuccinate without displacing an acetyl group.

*Diethyl benzeneazodiacetylsuccinate*,



is obtained as a pale yellow precipitate on adding sodium acetate to a dilute alcoholic solution containing benzenediazonium chloride and the diketonic form of diethyl diacetylsuccinate; it crystallises in lustrous, yellow leaflets melting at 108° and is soluble in the ordinary organic solvents. With concentrated sulphuric acid, it yields a clear yellow solution, whilst potassium permanganate or dichromate develops a violet coloration. Although the insolubility of the compound in cold, dilute alkalis seems to indicate that it has the diketonic constitution, yet the fact that it is not acted on by excess of the diazonium salt tends to show that it possesses the alternative keto-enolic formula,  $CO_2Et \cdot CAc(N:NPh) \cdot C(CO_2Et) \cdot CMe \cdot OH$ .

*Diethyl 1-phenyl-3-methylisopyrazole-4-5-dicarboxylate*,



produced by boiling the preceding compound with water for 10 hours, crystallises from dilute alcohol in almost colourless, transparent, monoclinic plates [ $a:b:c = 0.6072:1:0.9663$ ;  $\beta = 112^\circ 37'$ ] and melts at 51.5°; it is readily soluble in the ordinary organic solvents, but not in water. In small quantities, it may be distilled without decomposition; it is not attacked by concentrated sulphuric acid, and when reduced in alcoholic solution gives Knorr's pyrazoline reaction.

*1-Phenyl-3-methylisopyrazole-4:5-dicarboxylic acid*, obtained either by hydrolysing the preceding ester with acids or alkalis or by boiling the original azo compound with dilute caustic soda solution, melts at 247°; its isomeride, *1-phenyl-5-methylisopyrazole-3:4-dicarboxylic acid*, melts at 198° (Knorr and Laubmann, *Abstr.*, 1899, 409). The *silver salt*,  $AgC_{12}H_9N_2O_4$ , is obtained by treating the *acid ammonium salt* with silver nitrate; the acid is shown to be dibasic by titrating with standard caustic alkali in presence of phenolphthalein.

1-Phenyl-3-methylisopyrazole,  $\text{NPh} \begin{smallmatrix} \text{N}-\text{CMe} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix}$ , is obtained as an oil

when the preceding compound is heated above its melting point; it boils at  $255-265^\circ$  under a pressure of 744 mm. and possesses an odour like that of quinoline. The *methiodide* melts at  $287^\circ$ , the *platinichloride* crystallises in yellow plates with ragged edges and melts at  $198^\circ$ .  
G. T. M.

**Double Chloride of Copper and Antipyrine.** By M. C. SCHUYTEN (*Chem. Centr.*, 1899, ii, 37; from *Bull. Acad. roy. Belg.*, [iii] 37, 140-142).—The salicylate of copper and antipyrine (compare Abstr., 1899, i, 306) contains only one mol. of base. The chloride of copper and antipyrine,  $\text{CuCl}_2(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_2$ , prepared by mixing solutions of cupric chloride and antipyrine, crystallises in ruby needles, melts at  $145^\circ$  and dissolves in water, forming a greenish acid solution which gives the characteristic reactions of copper and antipyrine.  
E. W. W.

**Metallic Benzopyrines.** By M. C. SCHUYTEN (*Chem. Centr.*, 1899, ii, 38; from *Bull. Acad. roy. Belg.*, [iii], 37, 126-134).—The benzoates of iron, aluminium, copper, and uranium take up antipyrine in the largest quantities and retain it most stubbornly, but they do not form compounds of constant composition. Similarly, benzoic acid and the benzoates of magnesium, chromium, manganese, cobalt, nickel, zinc, silver, cadmium, gold, mercury, and lead form only more or less stable mixtures with antipyrine.

The properties and behaviour of the various substances obtained are described in the original paper.  
E. W. W.

**Constitution of Metallic Salipyrines.** By M. C. SCHUYTEN (*Chem. Centr.*, 1899, ii, 38; from *Bull. Acad. roy. Belg.*, [iii], 37, 135-139).—The capability of metallic salicylates of forming double compounds with antipyrine must be due to the presence of a hydroxyl group, since benzoates do not form such compounds. This property, however, is easily destroyed, as, for instance, by the presence of the groups characteristic of anhydrides, for the phthaleins do not combine with antipyrine. The salipyrines are divided into the following classes: (1) those of the type of the iron compound; (2) the magnesium, manganese, cobalt, nickel, zinc, and cadmium compounds; (3) the copper and lead compounds and (4) the aluminium, chromium, silver, gold, mercury and uranium compounds, which cannot be prepared by the usual methods. Constitutional formulæ for the compounds of the first three classes are given in the original paper.

E. W. W.

**Formation of Ring Compounds by Elimination of Aromatic Nitro-groups.** By ALFRED WERNER and TH. HERBERGER (*Ber.*, 1899, 32, 2686-2696. Compare V. Meyer, Abstr., 1889, 516; Turpin, Trans., 1891, 59, 714-725; and Kehrman and Messinger, Abstr., 1894, i, 55).—6-Nitro-3-phenyl-2:4- $\Delta^2$ -benzazoxazine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{N} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{C} \end{smallmatrix} \text{Ph}$ , prepared by the action of alcoholic potash on 2:4-dinitrophenylbenzenyl-

aminoxime (Werner, Abstr., 1894, i, 461), crystallises from chloroform in reddish-brown, pleochroic prisms, or from concentrated solution in bundles of yellow prisms or plates; the two modifications have the same composition, and often separate together from solution, and as the labile hydrogen atom is known to wander from the 4- to the 2-position, it is suggested that these may represent the two isomeric forms. The substance becomes dark red at 168° and melts at 173°; like all members of the series containing the NH group, it gives a blue solution with alcoholic potash (*Ber.*, 1886, 19, 1669).

Benzenylanilinoxime (Müller, Abstr., 1886, 875) was prepared by the action of aniline on benzhydroximic chloride. The 2:4-dinitrophenyl ether,  $\text{NHPh} \cdot \text{CPh} : \text{N} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ , prepared by the action of sodium ethoxide on an alcoholic solution of benzenylanilinoxime and dinitrochlorobenzene, crystallises from hot alcohol in orange-yellow prisms and melts at 150°; a colourless substance is also produced which crystallises from hot alcohol in long, quadratic prisms, melts at 173°, and has the composition of a nitrodiethoxybenzene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OEt})_2$ .

6-Nitro-3:4-diphenylbenzazoxazine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \text{---} \text{N} \\ \parallel \\ \text{NPh} \cdot \text{CPh} \end{smallmatrix}$ , crystallises from chloroform in well-formed, amber-yellow, rhombic prisms, and melts at 168°; only one modification was observed.

Dinitrophenyl-p-tolonylaminoxime,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ , crystallises from alcohol in sulphur-yellow, hexagonal prisms and melts at 174°. 6-Nitro-3-p-tolylbenzazoxazine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \text{---} \text{N} \\ \parallel \\ \text{NH} \cdot \text{C} \cdot \text{C}_6\text{H}_4\text{Me} \end{smallmatrix}$ , crystallises from chloroform in dark orange-red, rhombic prisms or tablets, melts at 185°, and is readily soluble in chloroform or acetone. The carbanilide crystallises from alcohol in long, sulphur-yellow, rhombic needles, and melts at 270°.

2:4-Dinitrophenyl-p-nitrobenzenylamininoxime,  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ ,  
 crystallises from alcohol in pale yellow needles and melts at 240°.

6-Nitro-3-p-nitrophenylbenzazoxazine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \text{---} \text{N} \\ \parallel \\ \text{NH} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{smallmatrix}$ , crystallises from acetone in dark-red needles, melts at 126°, and dissolves slightly in ether or alcohol.

p-Nitrobenzenylanilinoxime,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NHPh}) : \text{NOH}$ , crystallises from alcohol in lemon-yellow needles and melts at 183°. The 2:4-dinitrophenyl ether crystallises from alcohol in dark orange-red prisms and melts at 177°.

6-Nitro-4-phenyl-3-p-nitrophenylbenzazoxazine,  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \text{---} \text{N} \\ \parallel \\ \text{NPh} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{smallmatrix}$ ,  
 crystallises from chloroform in orange-yellow, hexagonal prisms and melts at 182°.

Dinitrophenyl-m-nitrobenzenylamininoxime crystallises from alcohol in long, sulphur-yellow prisms and melts at 222°. 6-Nitro-3-m-nitrophenylbenzazoxazine crystallises from acetone in orange-red, rhombic prisms and flakes, melts at 118°, is insoluble in alcohol, but dissolves in alcoholic potash, forming a dark blue solution.



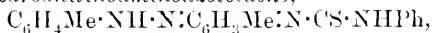
*m*-Nitrobenzenylanilinoxime, prepared by the action of aniline on *m*-nitrobenzhydroxamic chloride, crystallises from alcohol in yellow needles and melts at 158°; the 2:4-dinitrophenyl ether crystallises from acetic acid in lemon-yellow flakes, melts at 162°, and is soluble in acetone.

6-Nitro-4-phenyl-3-*m*-nitrophenylbenzazoxazine crystallises from chloroform in yellow flakes, dissolves slightly in alcohol or ether, and melts at 189°.

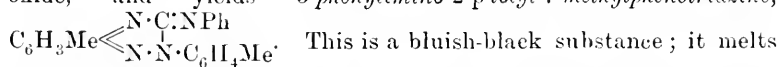
Benzylbenzenylanilinoxime,  $\text{NOH}\cdot\text{CPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , crystallises from alcohol in white flakes, melts at 120°, and dissolves readily in ether.

The 2:4-dinitrophenyl ether crystallises from alcohol in bunches of long, yellow needles, melts at 130°, and dissolves in ether or chloroform. 6-Nitro-3-phenyl-4-benzylbenzazoxazine crystallises from alcohol in long, greenish-yellow needles, melts at 136°, and dissolves readily in alcohol, chloroform, or light petroleum. T. M. L.

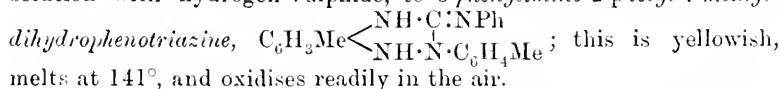
**Triazines from *o*-Aminoazo-compounds.** By MAX BUSCH (with LUDWIG HARTMANN; *Ber.*, 1899, 32, 2959—2972).—Carbanilino-aminoazotoluene (Goldschmidt and Rosell, *Abstr.*, 1890, 616) could not be made to undergo internal condensation with elimination of water, but thiocarbanilinoaminoazotoluene,



(which is formed from phenylthiocarbimide and *o*-aminoazotoluene in concentrated alcoholic solution, is yellow, and melts at 149°), loses hydrogen sulphide when treated in benzene solution with mercuric oxide, and yields 3-phenylimino-2-*p*-tolyl-7-methylphenotriazine,

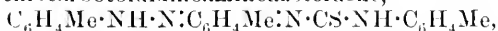


at 127.5°, and is basic in character; the brownish-red *hydrochloride*, with  $(\text{C}_{21}\text{H}_{15}\text{N}_3)_2\cdot 3\text{HCl}$ , melting at 98°, brown *platinichloride*, melting above 260°, and dark blue *picrate*, melting at 204°, were analysed. The triazine is converted by acid reducing agents, best in benzene solution with hydrogen sulphide, to 3-phenylimino-2-*p*-tolyl-7-methyl-



melts at 141°, and oxidises readily in the air.

A similar series of compounds was prepared from *p*-tolylthiocarbimide; thiocarbotohydinoaminoazotoluene,



is brownish-yellow, and melts at 155°. 3-Tolylimino-2-*p*-tolyl-7-methylphenotriazine is bluish-black, and melts at 147°, the *hydrochloride*, with  $1\frac{1}{2}\text{HCl}$ , is dark claret, and melts at 103°, the *platinichloride* is dark red, and the *picrate*, melting at 216°, is deep violet-blue; the corresponding *dihydrotriazine* is yellowish, and melts at 166—168°.

2-Tolylketo-7-methylphenotriazine,  $\text{C}_6\text{H}_4\text{Me}\begin{array}{c} \text{N}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me} \end{array}$ , is formed from *o*-aminoazotoluene and carbonyl chloride in benzene-toluene solution; it is red, melts at 168°, and forms salts which are decomposed by water; the dark claret *hydrochloride* melts at 154°. Alcoholic potash converts it into yellow ethyl *o*-toluenecarbazotolylcarb.

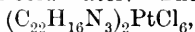
*amate*,  $C_6H_4Me \cdot NH \cdot N \cdot C_6H_4Me \cdot N \cdot CO_2Et$  (also formed from *o*-aminoazotoluene and ethyl chloroformate in the presence of pyridine and in benzene solution), which melts at  $94^\circ$  and has no basic properties; alcoholic ammonia converts it into the corresponding yellow *carbamide* melting at  $207^\circ$ , and aniline into the anilide (*carbanilinoaminoazotoluene*, *loc. cit.*). Acid-reducing agents convert it into the *di-hydroketotriazine*, which melts at  $146^\circ$ , and oxidises readily in the air; zinc powder and acetic anhydride convert it into the *acetyl* derivative of this,  $C_6H_4Me \cdot \begin{matrix} NH-CO \\ | \\ NAc \cdot N \cdot C_6H_4Me \end{matrix}$ , which melts at  $190^\circ$  and is stable in the air.

2-Phenylketonaphthatriazine, prepared by Goldschmidt and Rosell (*loc. cit.*) from benzeneazo- $\beta$ -naphthylamine and phenylcarbimide, is also formed from the benzeneazo- $\beta$ -naphthylamine and carbonyl chloride. With alcoholic potash, it yields benzeneazo- $\beta$ -naphthylamine, not a carbamate. The latter, *ethyl benzeneazo- $\beta$ -naphthylcarbamate*, can be prepared, though with some difficulty, from benzeneazo- $\beta$ -naphthylamine and ethyl chloroformate; it is orange-red, melts at  $110^\circ$ , and is converted by cold alcoholic potash into the ketotriazine.

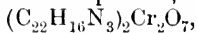
C. F. B.

**The Eighth and Ninth Isomerides of Rosinduline.** By FRIEDRICH KEHRMANN and P. FILATOFF (*Ber.*, 1899, 32, 2627—2633. Compare Abstr., 1898, i, 154, 155; 1899, i, 238, 525).—When well dried phenylnaphthaphenazonium nitrate (Abstr., 1897, i, 172) is added to about 5 times its weight of the strongest nitric acid, cooled to  $0^\circ$ , the solution allowed to remain at this temperature for 2—3 hours and then diluted with ice, a more or less crystalline precipitate, consisting of a mixture of two isomeric *mononitro*-derivatives, is deposited. These may be separated by the aid of cold alcohol, in which one is only sparingly soluble.

The sparingly soluble nitrate dissolves in warm alcohol, yielding a lemon-yellow, non-fluorescent solution, which, when boiled, undergoes decomposition; when its alcoholic solution is reduced with stannous chloride and concentrated hydrochloric acid and then allowed to cool, crystals of the stannochloride of the leuco-compound are deposited. This is converted into *aminophenylnaphthaphenazonium chloride* (*rosinduline* No. 8) by boiling with 25 per cent. alcohol, and aspirating air through the boiling solution, filtering and treating the residue in exactly the same manner until the residue consists of pale grey tin hydroxide. When recrystallised from alcohol, it forms short, glistening, violet prisms with a metallic lustre, and still retains  $1H_2O$  at  $110^\circ$ . Its aqueous solution has a greenish-blue, its alcoholic solution, a pure green, colour, and its solution in sulphuric acid is golden-yellow, but none of these exhibit fluorescence. The *nitrate*,  $C_{22}H_{16}N_3 \cdot NO_3$ , crystallises from alcohol in small, violet, glistening prisms sparingly soluble in cold water. The *platinichloride*,



is a sparingly soluble, green-black powder, and the *dichromate*,



a dark-green, crystalline powder insoluble in water.

When the readily soluble nitro-derivative is reduced and the product treated as above, a chloride (*isorosinduline* No. 8) is obtained; it crystallises from alcohol in long, violet prisms, dissolves in water, giving a deep-blue solution, in alcohol yielding a greenish-blue solution, and in sulphuric acid to a blood-red solution. The *platnichloride*,  $(C_{22}H_{16}N_3)_2PtCl_6$ , is a dark blue, and the *dichromate* a green, crystalline precipitate.

The constitutions of the two isorosindulines have not been established.

J. J. S.

**Nitro- and Amino-flavindulines.** By FRIEDRICH KEHRMANN and ZENAIDE KIKINE (*Ber.*, 1899, 32, 2633—2637).—When phenanthraquinone is treated with fuming nitric acid, it yields various nitro-derivatives (compare Anschütz and Schultz, this Journal, 1877, i, 210; Schmidt, *Abstr.*, 1879, 941; Strasburger, *ibid.*, 1884, 328; Schultz, *ibid.*, 1880, 814). The authors have isolated a *mononitro*-derivative melting at  $161^{\circ}$ — $162^{\circ}$ , and a *dinitro*-derivative, melting at  $279^{\circ}$ , which appears to be identical with the compound described by Graebe (*Abstr.*, 1873, 895); no mononitro-compound melting at  $257^{\circ}$  (compare Anschütz) could be found.

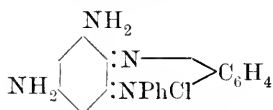
*Nitroflavinduline*,  $NO_2 \cdot C_{14}H_7 \llcorner \begin{smallmatrix} N \\ \text{NPhCl} \end{smallmatrix} \gg C_6H_4$ , is obtained when the mononitro-derivative melting at  $161^{\circ}$  is suspended in glacial acetic acid, mixed with the requisite amount of phenyl-*o*-phenylenediamine hydrochloride, and allowed to remain at the ordinary temperature until complete solution ensues, an operation requiring several days. It forms thick, amber-yellow prisms, readily soluble in water or alcohol, but insoluble in ether, its solutions being golden-yellow in colour and non-fluorescent. The *platinichloride*,  $(C_{26}H_{16}O_2N_3)_2PtCl_6$ , forms a reddish-yellow, crystalline precipitate practically insoluble in water, and the *dichromate* a flocculent precipitate of the same colour. When reduced with stannous chloride and hydrochloric acid, the nitro-compound is converted into the sparingly soluble stannochloride of the leuco-derivative of amino-flavinduline; the latter is then oxidised with ferric chloride, dissolved in water, treated with an excess of sodium acetate, filtered, and treated with solid sodium bromide, when *amino-flavinduline bromide*,  $C_{26}H_{18}N_3Br$ , separates in the form of dark green needles readily soluble in water and in concentrated sulphuric acid; the *dichromate*,  $(C_{26}H_{15}N_3)_2Cr_2O_7$ , forms a green, insoluble precipitate.

*2:7-Dinitroflavinduline*,  $C_{14}H_6(NO_2)_2 \llcorner \begin{smallmatrix} N \\ \text{NPhCl} \end{smallmatrix} \gg C_6H_4$ , obtained when dinitrophenanthraquinone is condensed with *o*-aminodiphenylamine hydrochloride, crystallises from acetic acid in small, lemon-yellow prisms, is readily soluble in cold water, but only sparingly in cold alcohol. *2:7-Diamino-flavinduline bromide*,  $C_{26}H_{19}N_4Br$ , crystallises in short, blackish-green prisms moderately soluble in water; the *dichromate* forms a dark green powder insoluble in water. J. J. S.

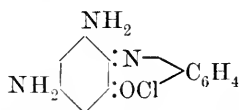
**Constitution of Oxazine Dyes, and Quadrivalent Oxygen.** By FRIEDRICH KEHRMANN (*Ber.*, 1899, 32, 2601—2611). [With KRAMER.]—*Isophenosuffranine chloride*,  $C_{18}H_{15}N_3Cl$ , is obtained by reducing 1:3-dinitro-5-phenyldihydrophenazine (*Abstr.*, 1893, i, 55) with

stannous chloride, oxidising a dilute acetic acid solution of the leuco-base so produced with atmospheric oxygen, and precipitating the dye with sodium chloride; it crystallises from water in greenish-black needles having a metallic lustre; its solution in alcohol or water is bluish-green. When dissolved in concentrated sulphuric acid, an orange coloration is produced; on diluting this solution with water, it becomes red, and then contains the diacid salt; on further dilution, or partial neutralisation, the green tint of the monacid salt is developed. The base is not liberated from its monacid salts by sodium carbonate or ammonia, and only partially by caustic alkalis. The *nitrate* crystallises in greenish-black, sparingly soluble needles. The *platinichloride* and the dichromate are obtained as green precipitates.

The colour base obtained by replacing the group :NPh in isosaffranine by oxygen or sulphur closely resembles this compound in chemical and physical properties; this resemblance, however, is not indicated by the formulæ commonly given to hydrochlorides of oxazines and thiazines, the oxy- and thio-analogues of isosaffranine being represented as paraquinonoid derivatives, whereas isosaffranine chloride must be an orthoquinonoid substance. If, however, it is assumed that oxygen and sulphur are quadrivalent in these salts (compare Collie and Tickle, *Trans.*, 1899, **75**, 710), then it becomes possible to give constitutional formulæ to these substances analogous to that of the nearly related isosaffranine chloride, as follows:



Isosaffranine chloride.

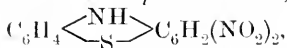


Diaminophenazoxonium chloride.

[With P. THOMAS.]—*Diaminophenoxazine*,  $\text{C}_{12}\text{H}_{11}\text{ON}_3$ , is obtained in the form of its stannochloride by reducing dinitrophenoxazine (Turpin, *Trans.*, 1891, **59**, 714) with stannous chloride.

*Diaminophenazoxonium bromide*,  $\text{C}_{12}\text{H}_{10}\text{ON}_2\text{Br}$ , prepared by oxidising an acetic acid solution of the preceding base with a current of air and then adding sodium bromide, crystallises from water in dull black leaflets; the aqueous solution has a green colour and a bitter taste. The base is liberated by caustic alkalis and sodium carbonate, but not by ammonium carbonate. The hydrobromide, when dissolved in concentrated sulphuric acid, gives a dark red solution which becomes brownish-yellow on dilution with water. The basic character of the compound persists even when the two amino-groups are acetylated.

[With L. SCHILD.]—3:5-*Dinitrophenothiazine*,



produced by heating picrylaminothiophenol with alcoholic sodium hydroxide, crystallises from alcohol in dark, reddish-brown needles with a green reflex. With alcoholic alkalis, it yields unstable bluish-violet salts which are decomposed by water; its solution in concentrated sulphuric acid is brownish-red.

3:5-*Diaminophenothiazine* is obtained by reducing the preceding compound with stannous chloride, and is identified by means of its

*diacetyl* derivative; the latter is produced by heating the stannochloride with acetic anhydride and dry sodium acetate; it crystallises from alcohol or glacial acetic acid in greenish-yellow needles insoluble in water.

3:5-Diaminophenazothionium chloride,  $C_{12}H_{10}N_2S \cdot Cl + H_2O$ , prepared by oxidising diaminophenothiazine with atmospheric oxygen or ferric chloride, crystallises from water in reddish-brown needles with green reflex. The *platinichloride* and *dichromate* are dark green precipitates. The base is liberated from its salts by caustic alkalis, but not by carbonates; on the other hand, it combines directly with carbon dioxide, and decomposes ammonium carbonate.

Alcoholic solutions of the bromide of the azoxonium base, and the chlorides of the azothionium base and isosaffranine have very similar absorption spectra, the blue and violet portions of the spectrum being completely obscured in each case. G. T. M.

**Aminouracil.** By ROBERT BEHREND and RICHARD GRÜNWARD (*Annalen*, 1899, **309**, 254—260).—Aminouracil,  $C_4N_2H_3O_2 \cdot NH_2$  (Behrend, *Annalen*, 1885, **229**, 38), is best obtained by reducing nitrouracil with ammonia and zinc dust. The *sodium* and *potassium* derivatives were prepared; the *sulphate* forms needles containing  $5H_2O$ , and the *nitrate* crystallises in lustrous leaflets with  $1H_2O$ . The *picrate* melts at  $147$ — $148^\circ$ ; the *acetyl* derivative sublimes without decomposing, and the *benzoyl* derivative crystallises from alcohol in leaflets melting at  $283$ — $287^\circ$ . M. O. F.

**Isomerism of the Methyluric Acids.** By EMIL FISCHER and FRIEDRICH ACH (*Ber.*, 1899, **32**, 2721—2749).—The usual formula for uric acid accounts for the existence of only four monomethyl derivatives; a fifth, however, has been obtained by von Loebe (Abstr., 1898, **74**, 128) and in this paper is given an account of a sixth isomeride.

$\zeta$ -Methyluric acid,  $C_6H_6O_3N_4$ , is obtained by heating a solution of potassium urate in dilute acetic acid with methyl iodide or chloride at  $100^\circ$ . It separates from boiling water in the form of short, microscopic prisms or rectangular tablets containing  $1H_2O$ . It dissolves in 600 parts of boiling water. When heated, it chars without melting. It gives the murexide test on treatment with nitric acid and reduces ammoniacal silver nitrate solution.

The *dipotassium* salt of the  $\zeta$ -acid is more soluble in dilute alcohol than that of uric acid. A *sodium hydrogen* salt,  $C_6H_5O_3N_4Na + 4H_2O$ , forms spherical aggregates of slender needles. The *barium hydrogen* salt, with  $4H_2O$ , forms aggregates of needles or prisms, and the *calcium hydrogen* salt, with  $2H_2O$ , forms beautiful, shining needles.

When  $\zeta$ -methyluric acid is oxidised with potassium chlorate and hydrochloric acid, it yields methylalloxan.

The methylation of  $\zeta$ -uric acid leads to the formation of products which differ with the mode of treatment. With excess of alkali and methyl iodide, hydroxycaffeine and tetramethyluric acid are produced at  $35$ — $40^\circ$ , and hydroxycaffeine and 1:3 dimethyluric acid at  $0$ — $20^\circ$ .

7-Chloro-2 : 5-dioxy-4-methylpurine,  $\begin{array}{c} \text{N}:\text{CCl}-\text{C}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{NH} \end{array} > \text{CO}$ , formed

when  $\zeta$ -methyluric acid is heated with phosphorus oxychloride at  $130^\circ$ , crystallises in glistening, colourless needles; it does not melt, but slowly decomposes above  $300^\circ$ . It dissolves in 105—110 parts of boiling water, and is sparingly soluble in acetone, chloroform, or ethyl acetate. It has fairly powerful acidic properties; the *potassium*, *sodium*, *ammonium*, and *barium* derivatives are described. It is only feebly basic.

2 : 5-Dioxy-4-methylpurine,  $\begin{array}{c} \text{N}:\text{CH}-\text{C}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{NH} \end{array} > \text{CO}$ , obtained by heating 7-chloro-2 : 5-dioxy-4-methylpurine with strong hydriodic acid and phosphonium iodide on the water-bath, separates from boiling water in clear, compact prisms or tablets containing  $\frac{1}{2}\text{H}_2\text{O}$ . The base decomposes without melting at a high temperature, dissolves in 35—40 parts of water, and is readily soluble in dilute acids, ammonia, or alkalis; the *hydrochloride* crystallises in compact, colourless prisms. The constitution of the substance was ascertained by exhaustive methylation, when a considerable quantity of 2 : 5-dioxy-1 : 3 : 4-trimethylpurine was produced.

7-Amino-2 : 5-dioxy-4-methylpurine,  $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)-\text{C}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{NH} \end{array} > \text{CO}$ , produced when 7-chloro-2 : 5-dioxy-4-methylpurine is heated at  $135\text{--}140^\circ$  with 18 per cent. ammonia, forms a white, crystalline powder which is very sparingly soluble in water and decomposes without melting when heated. The *hydrochloride* forms aggregates of white needles, and the *sulphate*, slender needles or long, acicular crystals which frequently form spherical aggregates. A solution of the base in hydrochloric acid gives a precipitate of slender, yellow, flexible needles on addition of auric chloride. The *potassium* and *sodium* derivatives were prepared. The base is at once destroyed by nitric acid and the solution exhibits the murexide reaction in a very marked manner.

When 7-chloro-2 : 5-dioxy-4-methylpurine is heated with dilute soda and methyl iodide, the halogen is eliminated and hydroxycaffeine is formed; in one instance, a substance was obtained having the composition of an iododioxymethylpurine, which yielded trimethyluric acid on treatment with acids. Chloro-4-methylxanthine is formed as a bye-product in the reaction between  $\zeta$ -methyluric acid and phosphorus oxychloride, and may be prepared by heating the foregoing chloro-dioxymethylpurine with phosphorus oxychloride at  $140\text{--}145^\circ$  for  $2\frac{1}{2}$  hours.

$\delta$ -Methyluric acid resembles the  $\zeta$ -derivative in general properties, solubility, hydration, behaviour on heating, and the appearance and solubility of its potassium salt, but differs markedly from it in its behaviour towards phosphorus oxychloride, which attacks it only with great difficulty at  $130^\circ$ , yielding, however, a small quantity of chloro-4-methylxanthine; the latter is more readily produced at  $140\text{--}145^\circ$ .  $\delta$ -Methyluric acid also yields tetramethyluric acid when heated with methyl iodide and soda at  $100^\circ$ .

$\zeta$ -Methyluric acid may be converted into the  $\delta$ -derivative, iether (1) by treatment with phosphorus oxychloride and hydrolysis of the

resulting chloropurino with 5 per cent. hydrochloric acid, when a mixture of the two isomeric acids is obtained, whence the  $\zeta$ -derivative may be removed by the use of phosphorus oxychloride; (2) by heating with hydrochloric acid for 9 hours on the water-bath; (3) by heating with normal potassium hydroxide in closed tubes at  $100^\circ$ , when a fairly complete conversion is effected.

A partial conversion of the  $\delta$ - into the  $\zeta$ -derivative has been accomplished by heating it at  $100^\circ$  with hydrochloric acid in a closed tube for 18 hours.

It is found that on oxidising the various methyluric acids with potassium permanganate or lead peroxide, the  $\alpha$ -,  $\zeta$ -,  $\delta$ -, and  $\beta$ -methyl derivatives yield the same methylallantoin, whilst the 1- and 6-methyluric acids afford a second; these products the authors distinguish by the prefixes  $\alpha$ - and  $\beta$ - respectively.

$\alpha$ -Methylallantoin melts and decomposes at  $248\text{--}249^\circ$  (corr.  $255\text{--}259^\circ$  [not  $225^\circ$  as stated by Hill (this Journal, 1876, 30, 509)]).  $\beta$ -Methylallantoin melts, when rapidly heated, at  $219\text{--}221^\circ$  (corr.  $225\text{--}227^\circ$ ), dissolves readily in hot water, and crystallises in large, colourless prisms containing  $1\text{H}_2\text{O}$ ; on reduction with hydriodic acid, it yields a methylhydantoin probably identical with that obtained by methylating hydantoin. A. L.

Inactive *b-p*-Nitranilineazobenzoylacetone [*p*-Nitrobenzene-azobenzoylacetone] and its Derivatives. By CARL BÜLOW (*Ber.*, 1899, 32, 2637—2649. Compare Abstr., 1899, i, 271).—*Inact-p-nitrobenzeneazobenzoylacetone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CHAcBz}$ , is obtained when an aqueous solution of *p*-nitroisodiazobenzenesodium (nitrosamine-red of the Badische Anilin- und Soda-Fabrik) and of sodium carbonate is mixed with a cold alcoholic solution of benzoylacetone, and the mixture allowed to remain for 12 hours. It crystallises from hot alcohol or acetic acid in brownish-yellow, jagged plates melting at  $141\text{--}142^\circ$ , and dissolves in acetone, benzene, or toluene; it is also soluble in dilute alkalis, and is reprecipitated on the addition of acids. It is not decomposed by  $\frac{1}{2}$  boiling with ammonium hydroxide, or by adding potassium dichromate, ferric chloride, or amyl nitrite to its solution in cold concentrated sulphuric acid. The *potassium* derivative,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CKAcBz}$ , forms large, reddish-violet, glistening plates.

*p*-Nitrobenzeneazobenzoylacetone methylimide,



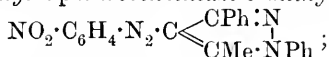
or  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}(\text{CPh}:\text{NMe})\cdot\text{CMe}\cdot\text{OH}$ , is slowly deposited as orange needles melting at  $155^\circ$  when an excess of aqueous methylamine solution is added to a warm, alcoholic solution of the condensation product. When the condensation product is boiled for an hour with an excess of aniline, then allowed to remain for 12 hours, and alcohol added, *p*-nitrobenzeneazobenzoylacetone phenylimide,



or  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}(\text{CPh}:\text{NPh})\cdot\text{CMe}\cdot\text{OH}$ , separates slowly in the form of long, orange-brown needles melting at  $146^\circ$ . It dissolves in cold acids, but on boiling, decomposition ensues; it is also soluble in dilute alkalis, yielding bluish-red solutions. Concentrated nitric acid at  $15^\circ$  converts *p*-nitrobenzeneazobenzoylacetone into a *nitrate*, which

crystallises in pale yellow needles; at  $27^{\circ}$ , nitration occurs, and a *p*-nitro-derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CHAc} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , is formed; this crystallises from boiling alcohol in yellow, felted needles melting at  $198$ — $199^{\circ}$ , and dissolves readily in benzene, in concentrated sulphuric acid, or alkalis.

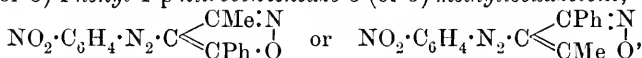
Two condensation products are formed when an acetic acid solution of equivalent quantities of *p*-nitrobenzeneazobenzoylacetone and phenylhydrazine is boiled for about half-an-hour. On the addition of a small quantity of water to the boiling solution, a product is obtained which, after several recrystallisations, melts at  $211^{\circ}$  to  $212^{\circ}$ , and is probably 1:3-diphenyl-4-*p*-nitrobenzeneazo-5-methylpyrazole,



the hot acetic acid filtrate from this product, on cooling, yields crystals of the second compound, which crystallises from alcohol in pale orange-red needles melting at  $166$ — $167^{\circ}$ , and is probably 1:5-diphenyl-4-*p*-nitrobenzeneazo-3-methylpyrazole.

3-(or 5)-Phenyl-4-*p*-nitrobenzeneazo-5-(or 3)-methylpyrazolone, obtained when an aqueous alcoholic solution of *p*-nitrobenzeneazobenzoylacetone and semicarbazide sulphate is boiled for 2 hours, forms orange, glistening crystals melting at  $241^{\circ}$ , insoluble in dilute acids, but soluble in warm dilute alkalis; in small quantities, it may be distilled without decomposition.

5-(or 3)-Phenyl-4-*p*-nitrobenzeneazo-3-(or 5)-methylisoxazolone,



is obtained when nitrobenzeneazobenzoylacetone and hydroxylamine hydrochloride are heated in aqueous alcoholic solution for 4—5 hours; it crystallises in orange needles, melts at  $192$ — $193^{\circ}$ , dissolves readily in alcohol, ether, or hot acetic acid, or in cold aromatic hydrocarbons. 3-(or 5)-*p*-Nitrophenyl-4-*p*-nitrobenzeneazo-5-(or 3)-methylisoxazolone, obtained from nitraniline-*p*-nitrobenzeneazonitrobenzoylacetone (melting at  $198$ — $199^{\circ}$ ) and hydroxylamine hydrochloride, crystallises in brownish needles melting at  $172^{\circ}$ .

2-*p*-Nitrophenyl-3-(or 5)-methyl-4-*p*-nitrobenzeneazo-5-(or 3)-phenylpyrazole, obtained when nitrobenzeneazobenzoylacetone is boiled for 60—80 hours with 15 per cent. hydrochloric acid, crystallises in brown, glistening plates melting at  $221$ — $222^{\circ}$ , and dissolves in concentrated sulphuric acid, yielding an orange-red solution. J. J. S.

**Hydrazones of Dithiocarbonates.** By MAX BUSCH and E. LINGENBRINK (*Ber.*, 1899, 32, 2620—2622).—Dithiocarbazine acid,  $\text{R} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS}_2\text{H}$ , and its esters,  $\text{R} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS}_2\text{R}'$ , react exclusively in the tautomeric form,  $\text{R} \cdot \text{NH} \cdot \text{N} : \text{C}(\text{SH})_2$  and  $\text{R} \cdot \text{NH} \cdot \text{N} : \text{C}(\text{SH}) \cdot \text{SR}$ ; acid hydrolysis decomposes the latter into phenylhydrazine and esters of dithiocarbonic acid.

The phenylhydrazone of dimethyldithiocarbonate is obtained as a yellow oil on digesting the sodium derivative of methyl phenyldithiocarbazine with methyl iodide in a closed vessel shielded from light; the hydrochloride is precipitated in a crystalline form by adding alcoholic hydrogen chloride to an ethereal solution of the oil. The



corresponding *dibenzyl* compound is prepared by heating benzyl phenyl-dithiocarbazine with benzyl chloride and sodium hydroxide in alcoholic solution ; it separates as a viscid, yellow oil. G. T. M.

**The Iodine Number of Proteids.** By F. BLUM (*Zeit. physiol. Chem.*, 1899, 28, 288—299).—The amount of iodine capable of entering into intramolecular union in a proteid (by means of the Blum-Vaube! method) is designated its iodine number.

Experiments on a variety of proteids are given ; thus, 8.5 to 9 is the number for serum-globulin ; 10—11 for serum-albumin ; 7 for egg-albumin ; 12.5 for the nucleo-proteid of the pig's thyroid ; the proteid regarded by the author as the specific proteid of the thyroid (thyrotoalbumin), has an iodine number of only 6. W. D. H.

**Reversible Liquefaction of Proteids.** By TSVETT (*Compt. rend.*, 1899, 129, 551—552).—The swelling and dissolution in water of proteids is known to be facilitated by the action of acids, alkalis, and salts, and various organic substances, such as resorcinol, catechol, phenol, chloral hydrate, &c., are found to have the same effect. Gelatin dissolves to the extent of 3—4 per cent. in an 80 per cent. aqueous solution of resorcinol, whilst, if added in excess, two distinct liquid layers are obtained, the upper layer being a solution of gelatin in aqueous resorcinol, and the lower layer a solution of aqueous resorcinol in gelatin. The phenomenon is reversible, since the gelatin may be obtained in its original state by dialysis or by addition of water. Casein, hæmoglobin, peptones, plastin, and chloroplastin behave in a similar manner with resorcinol, whilst negative results were obtained with myosin, egg-albumin, and legumin. N. L.

**Detection of Glutamic Acid amongst the Products obtained by decomposing Albumin of Animal Origin with strong Sulphuric Acid.** By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1899, 28, 123—131).—Although glutamic acid has been obtained in good yield by boiling animal proteids with hydrochloric acid and stannous chloride, it has not been isolated when sulphuric acid is the agent of hydrolysis ; this is because basic substances are formed at the same time in quantity more than sufficient to combine with the glutamic acid.

Casein was treated with sulphuric acid, a large part of the organic bases was precipitated with phosphotungstic acid, from the filtrate sulphuric and phosphotungstic acids were precipitated with just the required amount of baryta, and leucine and tyrosine were removed by crystallisation. The mother liquor, still slightly alkaline, was diluted, boiled, and saturated with copper carbonate ; it was then filtered, cooled, and precipitated with lead acetate ; the precipitate was collected and washed, suspended in water, and decomposed with hydrogen sulphide ; the filtered solution was concentrated to crystallisation. The crystals were dissolved in hot water and the solution saturated with copper carbonate, filtered, concentrated, and cooled ; the first few crystals that separated were free from copper, and were removed ; copper aspartate then crystallised. The mother liquor was decomposed with hydrogen sulphide, filtered, and concentrated, when

glutamic acid crystallised out. Some more of it is contained in the filtrate from the lead precipitate; in all, the casein yielded 1·8 per cent. of glutamic acid.

In the course of the investigation, a crystalline substance was obtained and analysed, which was apparently a compound of glutamic and aspartic acids,  $5C_5H_9O_4N, C_4H_7O_4N$ . C. F. B.

**Products of the Peptic Digestion of Fibrin.** By ERNST P. PICK (*Zeit. physiol. Chem.*, 1899, 28, 219—287).—This paper is the first of a series which appears to treat in a thorough way the properties, separation (by fractional precipitation with ammonium sulphate), analysis, &c., of the various products of the gastric digestion of fibrin. It is noticeable that in the ultimate analysis of proto- and hetero-albumose, with which the present paper is principally concerned, the numbers obtained, especially for carbon, differ considerably from those previously given by Kühne and Chittenden.

The following table compares the percentage composition of fibrin (Hammarsten) and the two proteoses just mentioned; the carbon and nitrogen are more, and the oxygen less, abundant than in the original fibrin.

	Fibrin.	Hetero-albumose.	Proto-albumose.
C.....	52·68	55·12	55·64
H .....	6·83	6·61	6·80
N .....	16·91	17·98	17·66
S.....	1·10	1·22	1·21
O.....	22·48	19·07	18·69

Both albumoses are carbohydrate-free, unlike fibrin, and both contain only easily separable sulphur. They differ from one another, not only in solubility, but also in the following ways: hetero-albumose contains 39, and proto-albumose 25, per cent. of its nitrogen in a basic form; proto-albumose yields tyrosine, indole, and scatole abundantly, hetero-albumose in traces only. Hetero-albumose yields abundance of leucine and glycocine; proto-albumose yields only a little leucine and no glycocine.

These two proteoses arise together from fibrin, but not one from the other. Both yield, on further gastric or pancreatic digestion, deuterio-albumoses A and B, and peptone B. Deuterio-albumose B, however, contains the carbohydrate radicle of the original fibrin, and must be looked on as a primary digestion product. The deuterio-albumose B, which comes from proto- or from hetero-albumose, contains no carbohydrate radicle, and is a secondary product, or probably a mixture of two or more ( $B_1, B_2$ , &c.). This confirms what has already been stated by Zunz (*Abstr.*, 1899, ii, 504). W. D. H.

**Products of the Decomposition of Hæmatin.** By WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1899, 28, 1—33).—In the preparation of hæmatin by Nencki's method, the yield can be increased by using amyl alcohol that has been employed already for the same purpose; the hæmin then obtained, however, is poorer in chlorine than is represented by the formula  $C_{32}H_{31}O_3N_4ClFe$ . In the conversion of

hæmin into hæmatin, the alkali must be allowed to act at the ordinary temperature; otherwise the product is poorer in carbon and hydrogen than the formula  $C_{32}H_{30}O_3N_4Fe$  requires, although the amounts of nitrogen and iron remain the same.

Attempts to eliminate HCl from hæmin and obtain a compound  $C_{32}H_{30}O_3N_4Fe$  by heating the former with aniline were unsuccessful.

The oxidation of hæmatin has been studied more carefully than hitherto (compare Abstr., 1899, i, 468), but no new products have been detected. With sodium dichromate (or calcium chromate) in acetic acid solution, the best result is obtained when 12 atoms of oxygen are used per mol. of hæmatin and the oxidation is effected at the ordinary temperature; about 40 per cent. is converted into the anhydride of tribasic hæmatic acid,  $C_8H_8O_5$ , and dibasic hæmatic acid,  $C_8H_9O_4N$  (Abstr., 1896, i, 516), of which the former is present in larger amount; 40 per cent. is obtained in the form of a substance insoluble in water and still containing iron, which yields small quantities of  $C_8H_8O_5$  when further oxidised with alkaline permanganate; a small quantity of carbon dioxide is also formed, and some ammonia, more of which is produced in proportion as the yield of  $C_8H_8O_5$  is greater and that of  $C_8H_9O_4N$  less. When the oxidising agent employed is potassium ferrieyanide in strongly alkaline solution, at first at the ordinary temperature, then on the water-bath, 8—12 atoms of oxygen being used, the iron separates as hydroxide, a little  $C_8H_8O_5$  is formed, and also a substance, insoluble in water, which much resembles hæmatin and again yields small quantities of  $C_8H_8O_5$  when subjected to further treatment. With ammonium persulphate (equal to 20 atoms oxygen) as the oxidising agent on the water-bath, ammonia and a little hydrogen cyanide are evolved, iron hydroxide is precipitated, and apparently succinic acid and traces of volatile acids are formed.

It is suggested that hæmatin may be regarded as constituted according to the scheme  $FeR_2R^1_2$ , where R and  $R^1$  are complexes containing each 8 atoms of carbon. Hæmatoporphyrin is then  $RR^1$ , and the products of the oxidation of hæmatin are  $FeR^1_2 + R + R$ .

C. F. B.

**Preparation and Products of Decomposition of Hæmatoporphyrin.** By WILLIAM KÜSTER and MARTIN KÖLLE (*Zeit. physiol. Chem.*, 1899, 28, 34—39. Compare Abstr., 1897, i, 232).—Hæmatoporphyrin is oxidised much less readily than hæmatin (preceding abstract) by sodium dichromate in acetic acid solution; the products are dibasic hæmatic acid,  $C_8H_9O_4N$ , and substances, insoluble in water, of which the composition corresponds approximately with  $C_{14}H_{14}O_8N_2$  and  $C_{14}H_{16}O_5N_2$ . Dibasic hæmatic acid is shown by titration with ammonia to be really monobasic; when the ammonium salt is boiled with aqueous caustic soda, not one, but two mols. of ammonia are eliminated, and a salt of tribasic hæmatic acid,  $C_8H_{10}O_6$ , is formed; the anhydride of this acid is the substance  $C_8H_8O_5$ .

In the preparation of hæmatoporphyrin from hæmin by Schaffcoff's method, a bye-product, insoluble in water, is obtained; this has approximately the composition  $C_{32}H_{36}O_5N_4$ .

C. F. B.

**Blue Pigment in Coral (*Heliopora Cœrulea*) and other Animal Organisms.** By ARCHIBALD LIVERSIDGE (*Chem. News*, 1899, 80, 29—31; 41—43).—The pigment in blue coral was isolated by treatment with hydrochloric acid to remove the calcium carbonate, and extraction of the residue with 75 per cent. alcohol or acetic, formic, or propionic acid. On evaporation of the solvent, a dull, dark green mass was obtained. The behaviour of the pigment with a very large number of solvents and reagents was investigated, but no crystalline product was obtained. Comparison with other blue animal pigments seemed to show that this substance was not identical with any of them. D. A. L.

**Pyocyanin, the Blue Colouring Matter of *Bacillus Pyocyaneus*.** By G. W. BOLAND (*Chem. Centr.*, 1899, ii, 265; from *Centr. Bakt. Parasitenk.*, [i], 25, 897—902).—Pyocyanin is best obtained from cultures of *Bacillus pyocyaneus* in peptone-agar agar or peptone-gelatin, as in these cases it is free from the fluorescent colouring matter which is always formed in cultures containing glycerol; it is extracted with chloroform. The solution in chloroform gradually becomes green and finally yellow, Fordos' pyoxanthin or pyoxanthose being formed; this change is also quickly effected by exposing the solution to sunlight. Since the aqueous solution under similar conditions remains unchanged, the formation of pyoxanthose is probably due to the liberation of chlorine, and this view was experimentally confirmed. The green colouring matter formed intermediately is a mixture of pyocyanin and pyoxanthose, and from a solution of these compounds in chloroform, hydrochloric acid (1:3) dissolves only the former whilst most of the latter may be extracted by sulphuric acid (1:3). Pyoxanthose crystallises in thick, microscopic needles. The reddish-brown colouring matter which is found in the culture together with pyocyanin is insoluble in chloroform, ether, alcohol, benzene, xylene, or carbon disulphide, but may be extracted by means of alkalis or barium hydroxide. Potassium hydroxide, which also extracts the fluorescent colouring matter, is the best solvent. The quantity of pyocyanin formed in the culture increases to a maximum in several days, remains constant for ten days and then gradually decreases, the reddish-brown colouring matter increasing proportionately until it alone is present.

*Bacillus pyocyaneus* probably forms only two colouring matters, pyocyanin and the fluorescent dye, the latter being also produced by many other bacteria. The pyocyanin is gradually oxidised to pyoxanthose by the oxygen of the air, whilst in the culture itself it is converted into a reddish-brown colouring matter. E. W. W.

**Ovarian Colloid.** By THEODOR PANZER (*Zeit. physiol. Chem.*, 1899, 28, 363—381).—The jelly-like substance which occurs in certain forms of ovarian cystoma has been named pseudomucin, paramucin, &c. It gives the ordinary proteid tests; it contains 93.1 per cent. of water, 5.7 per cent. of organic, and 1.2 per cent. of inorganic substances; among the inorganic constituents, sodium and chlorine are the most abundant. The principal organic constituent, the colloid, has the following percentage composition: C, 47.27; H, 5.86; N

8.40; S, 0.79; P, 0.54; ash, 6.43; iodine is absent. This agrees very well with Mitjukoff's analyses. The phosphorus is probably in the ash. By treatment with dilute sulphuric acid, a reducing but non-fermentable substance is obtained, which is probably allied to the reducing substance obtainable from cartilage. On decomposition, the proteid matter yields ammonia, leucine, humous substances, and traces of hexon bases.

W. D. H.

**Pseudo-nucleins.** By K. H. GIERTZ (*Zeit. physiol. Chem.*, 1899, 28, 115—122).—Artificial pseudo-nuclein is a salt-like combination of albumin with metaphosphoric acid; by dissolving it in water containing alkali, it is decomposed into alkali phosphate and albumin; the latter is probably present as a soluble alkali-albumin. The pseudo-nuclein from casein or vitellin contains no metaphosphoric acid which can be split off in this way, and is therefore not identical with the artificial nuclein.

W. D. H.

**Histon-like Substance from the Thymus.** By A. FLEROFF (*Zeit. physiol. Chem.*, 1899, 28, 307—312).—A histon-like proteid was obtained by extracting a thymus gland which had been under alcohol and ether with 2 per cent. sulphuric acid. Its percentage composition is C, 51.77; H, 8.06; N, 17.72; S, 1.99; O, 20.46. It gives the typical reactions of a histon. The acid also extracts a substance from the gland (parahiston) which is soluble after precipitation in excess of ammonia. A third substance was separated from parahiston during its purification with alcohol; it is sparingly soluble in alcohol, and precipitates a solution of Witte's peptone, but its nature was not determined.

W. D. H.

**Decomposition Products of Histon from Leucocytes.** By D. LAWROFF (*Zeit. physiol. Chem.*, 1899, 28, 388—398).—Histon prepared from thymus (see preceding abstract), when decomposed by hydrochloric acid, yields the three hexon bases, histidine, arginine, and lysine, which together account for 25 per cent. of its weight. Arginine is the most abundant. Both the hydrochloride and carbonate of lysine are dextrorotatory; so also are arginine and its hydrochloride. Details are given in full.

W. D. H.

**Histidine.** By ALBRECHT KOSSEL and FR. KUTSCHER (*Zeit. physiol. Chem.*, 1899, 28, 382—387).—Hedin (*ibid.*, 22, 193) states that histidine is optically inactive; this is not so, the free base being levorotatory  $[\alpha]_D - 39.74$ , whilst its salts are dextrorotatory,  $(C_6H_9O_2N_3, HCl, + 1.74, C_6H_9O_2N_3, 2HCl, + 5.3 \text{ to } 6.4)$ . There is, moreover, no difference between Hedin's and the authors' histidine in crystallographic and boiling point investigations. Full details of the examination of the crystals of histidine dichloride are given.

W. D. H.

**Decomposition Products of Conchiolin.** By G. WETZEL (*Chem. Centr.*, 1899, ii, 59; from *Centr. Physiol.*, 13, 113—114).—According to Krukenberg (*Abstr.*, 1885, 826), when conchiolin is heated with acids, leucine, leucinimide, and a substance which crystallises in transparent prisms are formed, but tyrosine is not obtained. The

author finds, however, that, by the action of acids on conchiolin prepared from the shells of *Mytilus galloprovincialis*, leucine, glycocine, and tyrosine are obtained, but not leucinimide. E. W. W.

**Lilienfeld's Synthesis of Peptone.** By MARTIA KLIMMER (*Pflüger's Archiv*, 1899, 77, 210—214).—Lilienfeld's so-called synthesised peptone was prepared and compared with true peptone. The artificial condensation product is not peptone; it does not give the biuret reaction, and is easily decomposed into its two constituents, phenol and aminoacetic acid. W. D. H.

**Antipeptone.** By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1899, 28, 88—97. Compare Abstr., 1898, i, 611; 1899, i, 179).—The paper, is largely controversial, and deals especially with the work and views of Kühne and of Siegfried. The author brings forward fresh experiments to support his contention that the so-called antipeptone is a mixture of several simple substances. W. D. H.

**Protamines.** By N. MORKOWIN (*Zeit. physiol. Chem.*, 1899, 28, 313—317).—The hitherto known protamines obtained from the sperm of various fishes have been named salmine, clupeine, scombrine, sturine, and arbacine. On decomposition, they yield the hexon bases, arginine, histidine, and lysine. A new protamine prepared from the sperm of the sea-hare (*Cyclopterus lumpus*) is now described; it is termed cyclopterine. It differs from the others by giving Millon's reaction, and also in percentage composition. It is not contaminated with peptone, although probably it is a loose compound of true protamine with a peptone-like material. It thus forms a link between the protamines and the proteids proper. W. D. H.

**Epinephrine.** By JOHN J. ABEL (*Zeit. physiol. Chem.*, 1899, 28, 318—362. Compare Abstr., 1899, i, 395).—Epinephrine, the substance in the suprarenals which raises blood pressure, is alkaloidal. It may be isolated from aqueous extracts of the gland as a benzoyl compound,  $C_{17}H_{14}O_4NBz$ ; on isolating the base from this, it loses most of its physiological activity. It yields a *hydrochloride*, *hydrobromide*, *picrate*, and a *triacetyl* derivative,  $C_{17}H_{12}O_4NAc_3$ , appears to be related to substances of the pyrrole or scatole group, and may have the constitution  $C_6H_4 < \begin{smallmatrix} NH \\ CMe \end{smallmatrix} > C \cdot CH(OH) \cdot CO \cdot C_6H_3(OH_2)$ . When fused with alkali, it yields scatole. On treatment with dilute alkalis, it yields a dark pigment, epinephric acid, and a product of basic nature, not defined at present, but having a coniine or pyridine-like smell. Normally, epinephrine possibly leaves the body in the urine as uroerythrin. W. D. H.

## Organic Chemistry.

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**The Wax of Bacillariaceæ and its Connection with Petroleum.** By GUSTAV KRÄMER and ADOLF SPILKER (*Ber.*, 1899, 32, 2940—2959).—Bacillariaceæ (diatoms) are known to contain drops of oil distributed in the plasma, and from peat, in which diatoms occur largely, 1·5—4 per cent. of a wax can be extracted which contains 10—11 per cent. of sulphur. In the Uckermark, to the west of Stettin, the bed, some 23 feet in thickness, of a lake, which was drained long ago, consists chiefly of diatoms, and from it a wax can be extracted. This melts at 50—70°, resembles ozokerite in appearance, contains C, 73·5; H, 11·2; S, 1·0, and ash, 2·4 per cent., from which it may be concluded that the wax contains oxygen and consists of esters of organic acids. Fuming nitric acid does not attack the wax in the cold, but dissolves 38 per cent. on heating; from the residue, lekene, which occurs in ozokerite (Beilstein and Wiegand, *Abstr.*, 1883, 1073), can be isolated.

These waxes much resemble ozokerite. The latter contains only 0·15 per cent. of sulphur, however; only traces of it are hydrolysed by alcoholic potash, and when it is distilled no water is formed and the gas evolved contains no oxides of carbon and but little hydrogen sulphide. Of the wax from the lake silt, on the other hand, about 10 per cent. undergoes hydrolysis; and on distillation of the peat-wax, water is formed and the gas evolved contains 10 per cent. of hydrogen sulphide together with carbon dioxide and monoxide. When ozokerite is distilled under a pressure of 20—25 atmos., the gas evolved consists of methane and olefines, along with traces of hydrogen sulphide and carbon dioxide; the gas obtained from the silt-wax in similar circumstances contains hydrogen sulphide and carbon dioxide and monoxide, and that from carnauba- and Japan-wax contains both oxides of carbon. In all cases, a large part of the distillate boils at 130—290°, and this fraction has the character of the paraffins; its composition is C, 84·4—85·0, and H, 15·1 per cent., and its molecular weight is 149—169 determined cryoscopically in benzene solution ( $C_{11}H_{24}$  requires C, 84·7; H, 15·3; molecular weight, 156). A similar fraction from petroleum (from the Tegernsee) had a like composition. It is further found that the composition of the strata overlying the ozokerite deposits of Eastern Galicia and the petroleum beds of the Tegernsee contain the same mineral constituents as the lake silt.

The following theory of the origin of petroleum is then developed. Lakes became filled up in the process of time with a growth of diatoms; over this growth other deposits were formed subsequently. The decay of the diatoms (which takes place very slowly) gave rise to ammonium carbonate, which hydrolysed the wax present; from the resulting acids, carbon dioxide and monoxide and water were eliminated, and ozokerite formed. Where the pressure was small and the temperature low, this was converted further into a comparatively low boiling petroleum; under greater pressure and higher temperature, the sulphur present

also exerting an influence, a petroleum was formed which contained a large proportion of viscid, high-boiling substances (probably formed by polymerisation of olefines); more extended action of the sulphur, and of atmospheric oxygen, gave rise to a petroleum containing much asphalt. Generally speaking, the petroleum would be absorbed by the sandy bed of the lake; occasionally it might be absorbed by a calcareous bed, a deposit of asphalt being thus formed. C. F. B.

Heptane contained in Grosny Naphtha. By K. W. CHARIT-SCHIKOFF (*Chem. Centr.*, 1899, ii, 474; from *J. Russ. Chem. Soc.*, 1899, 31, 552—554).—The benzene boiling at 84—100°, obtained from the naphtha of Grosny, contains an *isoeptane*,  $C_7H_{16}$ , which boils at 90.5—91.5°, and has a sp. gr. 0.7158 at 15°. This naphtha only contains a very small amount of normal heptane. The interpretation of the curves representing relationships of boiling point and specific gravity is discussed in the original paper, the author inclining to Aschan's, rather than to Markownikoff's, views. E. W. W.

Action of Acetylene on Oxides of Copper. By FRANK A. GOOCH and DE FOREST BALDWIN (*Amer. J. Sci.*, 1899, [iv], 8, 354—358). Compare Erdmann and Köthner, *Abstr.*, 1899, i, 21).—Several errors in calculation are pointed out in Erdmann and Köthner's communication. The experiments have been repeated, and the conclusion arrived at is that Erdmann and Köthner's "Kupferacetylen" is nothing less than a hydrocarbon or hydrocarbons mixed with copper or an oxide of copper. The amount of copper found varies considerably (1.54 to 24.21 per cent.) with the conditions of the experiment. When cuprous oxide is employed, a temperature of 225° is the most favourable; similar results may be obtained with cupric oxide, but copper itself is not acted on until much higher temperatures are reached.

Oxide of silver is acted on at the ordinary temperature, and, as a rule, an explosion occurs. J. J. S.

NOTE.—The same conclusion as to the nature of Erdmann and Köthner's compound has been arrived at by Alexander (*Abstr.*, 1899, i, 843). J. J. S.

Preparation of Tetrachloromethane. By E. SERRA (*Gazzetta*, 1899, 29, ii, 353—354).—Details are given of the method employed for the preparation of tetrachloromethane free from carbon disulphide and from chloroform, which are very difficult to entirely remove.

T. H. P.

Isomeric Compounds,  $C_6H_8O_4N_4$ , from Acetylmethylnitrolic Acid. By CARL STEFFENS (*Annalen*, 1899, 309, 241—253).—Acetylmethylnitrolic acid,  $COMe \cdot C(NO_2) \cdot NO_2$ , obtained by oxidising acetone with nitric acid, yields two compounds having the empirical formula  $C_6H_8O_4N_4$ ; one melts at 191°, and is produced by converting acetylmethylnitrolic acid into nitromethylglyoxime, and heating the latter with sodium hydrogen carbonate (Behrend and Schmitz, *Abstr.*, 1894, i, 109), whilst the other, melting at 140°, is derived by the agency of hydroxylamine from the product of heating acetylmethylnitrolic acid



(Behrend and Tryller, Abstr., 1895, i, 201). The author has attempted to establish the constitution of these two substances.

The derivative melting at  $191^{\circ}$ , referred to as Schmitz's compound, probably has the constitution represented by the formula  $\text{NOH}\cdot\text{CMe}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{N} \end{smallmatrix}\text{C}\cdot\text{CMe}\cdot\text{NOH}$ . The hydrochloride is decomposed by hot water, yielding the original substance, which dissolves in hot hydrochloric acid, liberating carbon dioxide; the remaining products are  $\alpha$ -isonitrosopropionic acid, ammonia, hydroxylamine, and acetic acid. The *diacetyl* derivative crystallises from alcohol in needles and melts at  $141^{\circ}$ ; the *dibenzoyl* derivative becomes brown at  $200^{\circ}$  and melts at  $220$ — $225^{\circ}$ , when it decomposes. The compound dissolves in alkali (2 mols.), and is reprecipitated by acids from a freshly prepared solution, but after an interval, acids do not yield a precipitate; it immediately reduces potassium permanganate.

The isomeride called Tryller's compound may have the constitution  $\text{NOH}\cdot\text{CMe}\cdot\text{C}\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}\text{C}\cdot\text{CMe}\cdot\text{NOH}$ . The hydrochloride readily yields

the original substance, which gives rise to carbon dioxide, oxalic acid, ammonia, hydroxylamine, and acetic acid when treated with boiling acids; there is produced also a small quantity of a volatile ketone, probably the ketone of which Tryller's compound is the dioxime. The *dibenzoyl* derivative crystallises in slender, white needles and melts at  $155.5$ — $156.5^{\circ}$ . The *anhydride*,  $\text{C}_6\text{H}_6\text{O}_3\text{N}_2$ , obtained by acidifying a solution in caustic soda which has been boiled for some time, crystallises from alcohol in lustrous, yellowish leaflets and melts at  $188$ — $190^{\circ}$ , becoming brown at  $150^{\circ}$ .  
M. O. F.

**Phosphoric Esters.** By JACQUES CAVALIER (*Ann. Chim. Phys.*, 1899, [vii], 18, 449—507. Compare Abstr., 1894, i, 484; 1895, i, 638; 1896, ii, 590; 1897, i, 310; 1898, i, 616, ii, 499; 1899, i, 558, ii, 13, 55).—A detailed account of work already published.

G. T. M.

**Manufacture of Glycerophosphate.** By MARCEL GUÉDRAS (*Chem. Centr.*, 1899, ii, 626; from *Mon. Sci.*, [iv], 13, 11, 577—580).—Commercial glycerophosphate,  $\text{CaPO}_3\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2$ , prepared by heating phosphoric acid with glycerol for a day at  $150^{\circ}$  and then for 3 days at  $115$ — $125^{\circ}$ , and treating the glycerophosphoric acid with milk of lime, is alkaline towards litmus, but neutral to phenolphthalein, dissolves in about 25 parts of water, leaving a small quantity of insoluble calcium phosphate, and is precipitated from its aqueous solution by heating. Boiling alcohol usually extracts some glycerol and phosphoric acid. Sodium and potassium glycerophosphates are syrupy liquids. The magnesium salt is a powder, and has properties similar to those of the calcium salt. The iron salt, prepared by digesting crude glycerophosphoric acid with iron dust below  $60^{\circ}$ , crystallises in leaflets which have a golden lustre. Quinine glycerophosphate,  $\text{C}_3\text{H}_7\text{O}_2\cdot\text{O}\cdot\text{PO}(\text{OH})_2(\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2)_2 + 4\text{H}_2\text{O}$ , is slightly soluble in water, more so in alcohol, and may be used as a substitute for quinine sulphate.  
E. W. W.

**Esters of Tungstic Acid.** By EDGAR F. SMITH and CLAUDE DUGAN (*J. Amer. Chem. Soc.*, 1899, 21, 1016—1017. Compare Goessmann, *Annalen*, 1857, 101, 218; Maly, *ibid.*, 1866, 139, 240).—When Maly's method is employed for the preparation of esters of tungstic acid, the products obtained consist of a mixture of hydrated tungstic acid and an incompletely esterified product: for example, with tungsten oxy-chloride and isobutyl alcohol, a product,  $3\text{WO}_3 \cdot 2\text{H}_2\text{O} + \text{WOCl}_2(\text{OC}_4\text{H}_9)_2$ , was obtained, which was soluble in dry ether, but was reprecipitated on the addition of pure ethyl alcohol. J. J. S.

**Action of Water on certain Fatty Acids.** By EDWIN DE BARR (*Amer. Chem. J.*, 1899, 22, 333—349).—The author has studied the rate of interaction of water with certain halogenated fatty acids at  $150^\circ$ , 3 mols. of water being used for each halogen atom present. Tables of values are given and curves plotted, which show the rate of displacement of the halogen atoms from  $\gamma$ -chlorobutyric,  $\beta$ -chloropropionic, trichloroacetic,  $\beta$ -chlorobutyric, chloroacetic, dichloroacetic,  $\alpha$ -chloropropionic,  $\alpha$ -bromopropionic,  $\alpha$ -bromobutyric, and  $\alpha$ -chlorobutyric acids; the relative ease with which the halogen is removed from the various acids is given by the order in which these are named. This order is, except in the cases of mono-, di-, and trichloroacetic acids, not the same as that of the affinity constants. Most of the acids begin to undergo secondary change before the displacement of the halogen is complete; the relative stability of the compounds at  $150^\circ$  under pressure and in presence of hydrogen chloride appears to be in the order,  $\alpha$ -bromopropionic (7.06),  $\alpha$ -chlorobutyric (7.50),  $\alpha$ -bromobutyric (9.25),  $\alpha$ -chloropropionic (11.41), dichloroacetic (17.76),  $\beta$ -chlorobutyric (37.38), chloroacetic (47.11),  $\beta$ -chloropropionic (50.49), trichloroacetic (100.00), and  $\gamma$ -chlorobutyric acids (100.00), the numbers attached to each acid showing the percentage of halogen displaced before decomposition begins. On comparing this list with the foregoing, it appears that those acids which are most stable react the most rapidly with water, whilst those which are least stable react most slowly.

It appears, moreover, that with the  $\alpha$ -acids containing the same halogen, the rate of displacement of the latter diminishes in passing from acetic acid to its higher homologues; the same holds true with the  $\beta$ -acids, and a similar law regulates the total amount of transformation occurring before decomposition begins. It is especially noteworthy that the further a halogen atom is removed from the carboxyl group in the same acid, the more easily is it displaced under the influence of water; thus, the amount of halogen replaced after half an hour is 4.42 per cent. of the total in the case of  $\alpha$ -chloro-, and 41.5 per cent. in the case of  $\beta$ -chloro propionic acid.

$\beta$ -Chloropropionic acid is best prepared by the action of chlorine on  $\beta$ -iodopropionic acid, and melts at  $61^\circ$ , not at  $35.5^\circ$  to  $58^\circ$  as has formerly been stated; it boils at  $204^\circ$ .  $\beta$ -Chlorobutyric acid, prepared by saturating an ethereal solution of crotonic acid with hydrogen chloride at  $0^\circ$ , and subsequently leaving it in a sealed tube for 24 hours at the ordinary temperature, melts at  $16$ — $16.5^\circ$ , boils at  $116^\circ$  under 22 mm. pressure, and is entirely free from  $\alpha$ -acid.  $\gamma$ -Chloro-

butyric acid, prepared similarly from trimethylenecarboxylic acid, melts at 12° and boils at 196° under 22 mm. pressure. W. A. D.

**Electrolytic Oxidation of Succinic Acid.** By CHARLES H. CLARKE and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, **21**, 967—972).—The electrolytic oxidation of succinic acid in solutions containing known quantities of sodium hydroxide and of alcohol, has been studied. A divided cell was employed and a current density of from 0.024 to 1.55 ampères per 100 sq. cm. of anode surface. The products found were tartaric, oxalic, and carbonic acids, oxygen, carbon monoxide, ethylene, and methane, together with some aromatic substances. A colouring matter, soluble in ether and melting at 178°, has also been isolated. J. J. S.

**Separation and Purification of Sugars.** By OTTO RUFF and GERHARD OLLENDORFF (*Ber.*, 1899, **32**, 3234—3237).—Phenylbenzylhydrazine is better adapted for the isolation of sugars than phenylhydrazine itself, because of the ready formation and insoluble character of the hydrazones produced, and this substance has already been employed by Lobry de Bruyn and Alberda van Ekenstein (*Abstr.*, 1896, **i**, 588; 1897, **i**, 41). 1-*Xylosephenylbenzylhydrazone* melts at 99° (corr.), and dissolves in about 1000 parts of water. d-*Arabinosephenylbenzylhydrazone* melts at 174° (corr.), and is almost insoluble in water. The corresponding hydrazone of dextrose melts at 165° (corr.), and not at 150° as stated by these authors. The sugars are best regenerated from these hydrazones by treatment with formaldehyde, removal of the formaldehydephenylbenzylhydrazone by ether, and repeated evaporation of the solution to remove the excess of formaldehyde.

*Formaldehydephenylbenzylhydrazone* crystallises in white needles melting at 41°. A. H.

**Isomaltose.** By HENRI POTTEVIN (*Ann. de l'Inst. Pasteur*, 1899, **13**, 796—800).—From a solution of pure maltose and a non-reducing dextrin, the author has prepared an osazone which melts at 154° and crystallises in tufts of very slender needles. From this fact, and a consideration of previous work, he concludes that Lintner's isomaltose is a mixture of maltose and a dextrin (compare Ling and Baker, *Trans.*, 1895, **67**, 704, 739; 1897, **71**, 511; Brown and Morris, *Trans.*, 1895, **67**, 709). H. R. LE S.

**Crystallised Melibiose.** By ARMINIUS BAU (*Chem. Centr.*, 1899, **ii**, 526; from *Woch. Brauerei*, **16**, 397—400).—Melibiose was prepared by fermenting a solution of melitriose by means of a pure culture of a top-fermenting yeast. After decolorising the solution of the product with animal charcoal, it was evaporated and the melibiose precipitated from the residual syrup after filtering, by means of ether and purified by conversion into the barium compound, &c. Melibiose forms triclinic crystals containing 2H<sub>2</sub>O, is not hygroscopic, and is not changed by exposure to the air; it is easily soluble in water or methyl alcohol, and, like its aqueous solution, decomposes at 80°. It sinters at 82—83°, partially melts at 84—85°, and has a specific rotatory power  $[\alpha]_D +129.38'$  at 20°; freshly prepared solutions give a

slightly lower value for the last constant. Its power of reducing Fehling's solution, calculated on the dry substance, is only 92—95 per cent. as much as that of maltose, and it is neither hydrolysed nor fermented by top-yeasts, but is decomposed by bottom-yeasts, forming dextrose and *d*-galactose, which are completely fermented.

E. W. W.

**Rhamninoase.** By CHARLES TANRET and GEORGES TANRET (*Compt. rend.*, 1899, 129, 725—728).—It has been previously shown that xanthorhamnin, the glucoside of *Rhamnus infectoria*, is converted by the action of dilute acids into a mixture of rhamnetin, rhamnose, and galactose, the last-named compounds being themselves the products of hydrolysis of an intermediate saccharose, for which the name *rhamninoase* is now proposed. Rhamninoase, which is best obtained by the action of the ferment rhamnase, or, as it is more properly termed, rhamminase, on xanthorhamnin at 70°, is slowly hydrolysed by dilute acids into two mols. of rhamnose and one of galactose. It has a slightly sweet taste, and is soluble in all proportions in water, and very soluble in strong alcohol. It has a rotatory power  $[\alpha]_D - 41^\circ$ , and melts and slowly decomposes at 140°; it has not been obtained crystalline. Rhamninoase has one-third the reducing power of dextrose. Ordinary yeast, invertase, emulsin, and the ferments of *Aspergillus* have no action on it. No insoluble osazone or phenylhydrazone could be obtained from it. When treated with sodium amalgam in the cold, rhamninoase takes up two atoms of hydrogen and is converted into a new sugar, *rhamminite*,  $C_{18}H_{34}O_{14}$ , which has a rotatory power  $[\alpha]_D - 57^\circ$ , and yields rhamnose and dulcitol on hydrolysis. Rhamninoase is oxidised by nitric acid to mucic and galactonic acids, and by bromine to *rhamminotronic acid*,  $C_{18}H_{32}O_{15}$ . This acid is monobasic and bears the same relation to rhamninoase that lactobionic acid does to lactose. It has a rotatory power  $[\alpha]_D - 94^\circ$ , but does not reduce Fehling's solution; both it and its salts are anorphous. On hydrolysis, it yields two mols. of rhamnose and one of galactonic acid.

N. L.

**Constitution of Starch.** By WIKTOR SYNIEWSKI (*Annalen*, 1899, 309, 282—315. Compare Abstr., 1898, i, 551).—From experiments with potato starch, the author draws the following conclusions:

1. Potato starch granules consist of an individual substance having the empirical formula  $C_6H_{10}O_5$ .

2. Hydrolysis of potato starch can proceed in two ways, namely, carbinol-hydrolysis, in which addition of water to the anhydride of two carbinol groups takes place, and carbonyl-hydrolysis, in which at least one of the two groups forming the anhydride is a carbonyl radicle.

3. The compound obtained from potato starch by the action of boiling water under atmospheric or increased pressures, caustic potash, or sodium peroxide, is the result of carbinol-hydrolysis; it does not reduce Fehling's solution.

4. The simplest product of carbinol-hydrolysis is amylogen,  $C_{54}H_{96}O_{48}$ . The molecules of starch, and of all products of carbinol-hydrolysis standing between starch and amylogen, consist of a number of amyl-

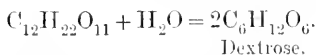
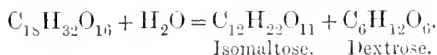
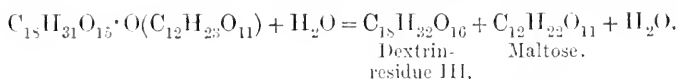
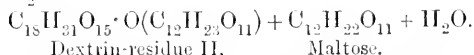
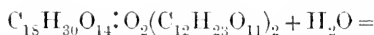
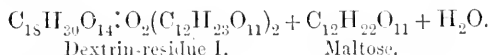
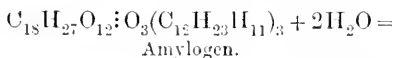
ogen molecules associated in the form of anhydrides by elimination of water from carbinol groups.

5. The composition of all such compounds may be expressed by the general formula  $(C_{54}H_{96}O_{38})_n - (3n - x)H_2O$ , in which  $n$  is unknown, and  $x$  is variable from 0 to  $3n$ .

6. Amylogen consists of three maltose residues, combined with a dextrin containing 18 atoms of carbon. The dextrin is composed of three glucose residues, of which two are in the form of an isomaltose residue.

7. The first stage in the hydrolysis of amylogen is the separation of the maltose molecules from one another and from the dextrin; further action of malt extract on the latter resolves it into glucose and isomaltose, which finally yields a further quantity of glucose.

8. Diastatic hydrolysis of amylogen gives rise to intermediate products, the changes being represented by the following equations:



9. Diastatic decomposition of those products of carbinol-hydrolysis of starch which contain many amylogen molecules yields a large number of dextrinous compounds, of which those containing the dextrin-residues I, II, and III are typical.

The author uses the name dextrin for all products of starch hydrolysis excepting sugars, and indicates as amylo-dextrins those which proceed from starch by carbinol-hydrolysis, and are therefore indifferent towards Fehling's solution, and develop the familiar starch blue with a solution of iodine in potassium iodide; the residual dextrin produced from amylo-dextrin by eliminating all the maltose is called "*Grenz-dextrin*." Dextrins between the latter and amylo-dextrins are called maltodextrins, and those derived from "*Grenz-dextrin*" by withdrawing dextrose residues are called glucodextrins.

M. O. F.

**Preparation of Starch Solutions and Separation of Starch Granules from such Solutions.** By HERMANN RODEWALD and A. KATTEIN (*Chem. Centr.*, 1899, ii, 419; from *Sitzungsber. Akad. Wiss. Berlin*, 24, 628—630).—When a solution of iodine in potassium iodide

is poured over potato, wheat, or rice starch and the mixture (which should contain 15 parts of iodine and 200—300 of water for every 100 of starch) heated for 15 minutes at  $130^{\circ}$ , a greenish-brown liquid is formed which consists mainly of excess of iodine solution with very small quantities of starch iodide and some sugar. The starch iodide grains, when examined under the microscope, appear to have been changed, and are soluble in water. The starch iodide may be separated by dialysing, and the blue solution so obtained forms a clear filtrate. This solution contains about 2 per cent. of the iodide and an amount of iodine corresponding with 14.3—14.85 per cent. of iodine in the iodide. When the solution is evaporated over a naked flame, the starch iodide separates and iodine is liberated; the latter may be removed by treatment with steam, and a clear or very slightly turbid solution of starch is then obtained. When the solution is slowly cooled, a white precipitate is formed, and this, when examined under the microscope, appears to consist of almost spherical starch granules. A similar precipitate is formed by all varieties of starch. The filtrate contains starch and gives an intense blue coloration with iodine; the blue compound may be separated by adding potassium iodide.

The starch granules which separate from the solution also give a blue coloration with iodine, and after drying are insoluble in cold water, and are only gelatinised with difficulty by boiling water. Potassium hydroxide also reduces the granules to paste. E. W. W.

**Saccharification of Starch.** By HENRI POTTEVIN (*Ann. de l'Inst. Pasteur*, 13, 1899, 665—688).—The dextrins obtained from starch by the action of amylase may be divided into three groups. (1) Achroodextrins, (2) amyloextrins, and (3) erythroextrins. With the first, starch produces no coloration, but with the second, a blue, and with the third a red coloration is obtained. No red coloration is produced when starch is added to a mixture of achroodextrin and amyloextrin, so that Solomon's statement that erythroextrins do not exist, but are mixtures of achroodextrins and amyloextrins is erroneous. Musculus' statement that amyloextrins in concentrated solutions give a blue coloration with starch and a red coloration in dilute solutions is also erroneous, because, whatever the dilution, a blue colour is always produced. Amyloextrin itself is not a single substance, for by careful precipitation with alcohol two dextrins have been obtained from it. The first,  $\alpha$ -amyloextrin, gives opalescent solutions, which on warming become somewhat viscous, but on cooling again become opalescent. Its blue compound with iodine is readily precipitated by a 1 per cent. solution of sodium chloride. The second, or  $\beta$ -amyloextrin, gives solutions which are viscous in the cold, and its compound with iodine is not precipitated by even a 20 per cent. solution of sodium chloride. The formation of dextrin from starch by the action of amylase is quite independent and distinct from the formation of maltose from the dextrin, for a solution may be prepared in which the formation of dextrin is still going on whilst that of maltose has completely stopped.

When amylase acts on starch, the rate of saccharification rapidly

decreases. This is due to the fact that the starch granules are not all of the same size, the larger ones being readily attacked by amylase, whereas the smaller are only attacked with difficulty.

H. R. LE S.

**Maltodextrin.** By HENRI POTTEVIN (*Ann. de l'Inst. Pasteur*, 1899, 13, 728—734).—The method of fermentation adopted by Brown and Morris to show that maltodextrin is not fermentable with yeast, is here objected to, since no precautions were taken to render the fermenting liquid aseptic, or to prevent the subsequent introduction of microbes during the fermentation. Using carefully sterilised and aseptic solutions, the author confirms the statement of Brown and Morris that maltodextrin is not fermentable, but points out that this is no evidence that maltodextrin is not a mixture, because a mixture can be made of pure maltose and a suitable dextrin, which, like maltodextrin, is not fermentable with yeast. Dextrins soluble in 70 per cent. alcohol retard the fermentation of maltose much more than those which are soluble in more dilute alcohol solutions. By careful fractional precipitation of a solution of maltodextrin by means of alcoholic solutions of varying strengths, precipitates of different composition are obtained, those obtained by precipitation with 58 per cent. alcohol consisting of 20 per cent. of maltose and 80 per cent. of dextrin, whereas with 94 per cent. alcohol the precipitate contains 70 per cent. of maltose and 30 per cent. of dextrin. A mixture of pure maltose and a dextrin (soluble in 70 per cent. alcohol) dialyses in exactly the same way as a solution of maltodextrin. The mere fact that maltodextrin dialyses as a whole is therefore no proof that it is a single substance.

Those dextrins soluble in dilute alcohol dialyse more quickly than those which are only soluble in strong alcohol.

H. R. LE S.

**Preparation and Estimation of Glycogen.** By ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 701—705).—The process described, which serves for both the preparation and estimation of glycogen, is based on the fact that the nitrogenous substances with which glycogen is associated are completely precipitated by mercuric acetate in neutral solution. The well-bruised liver, muscle, or other material is thoroughly extracted with boiling water (addition of acid or alkali serves no useful purpose) and the liquid concentrated by evaporation, mixed with a little potassium acetate and a slight excess of mercuric acetate, filtered, and poured into an equal volume of 85 per cent. alcohol. The precipitated glycogen is purified by repeated solution in water and reprecipitation with alcohol, washed with a mixture of alcohol and ether, and finally dried at 110—120°. Glycogen is thus obtained as a perfectly homogeneous substance having the composition  $(C_6H_{10}O_5)_n$ . It is not truly soluble in water, since it is more or less completely separated from the liquid by filtration. In the presence of a trace of salts, it is wholly insoluble in 36 per cent. alcohol. Glycogen is not hydrolysed by heating at 100° with 3 per cent. potassium hydroxide solution or with 5 per cent. acetic acid, but when heated with 5—6 per cent. mineral acid at 115—120°, it is converted into a mixture of sugars having a reducing power slightly

greater than that of dextrose. Glycogen from the human liver yields products having a notably higher reducing power than those obtained from rabbit's liver, and from this and other considerations it is concluded that different varieties of glycogen are contained in the different organs of the same animal and also in the same organs of different animals. N. L.

**Composition of the Gum of Grevillea Robusta.** By RÆSER and PUAX (J. Pharm., 1899, [vi], 10, 398—400).—The fresh gum is soft, and of a whitish colour, but on keeping it becomes hard, and of a yellowish, and often of a reddish, colour. It is odourless and possesses an astringent taste. It entirely dissolves in water, from which it is precipitated by 95 per cent. alcohol, and by basic lead acetate, after the addition of ammonia, until slightly alkaline. Its aqueous solution reduces Fehling's solution, and when warmed with ferric chloride, its colour deepens, but no precipitate is produced. When the gum is treated with mineral acids, galactose and arabinose are produced. A complete analysis of the gum is given. H. R. LE S.

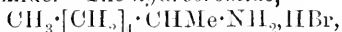
**Nitroacetone.** By AD. LUCAS (Ber., 1899, 32, 3179—3182. Compare Abstr., 1899, i, 401 and 433).—When silver nitrite is agitated for 24 hours with a dilute ethereal solution of iodoacetone, the nitroacetone produced remains insoluble, whilst the impurities dissolve; the nitroacetone, separated and dissolved in a larger quantity of ether, crystallises from the concentrated solution in well defined plates, melts at  $49^{\circ}$ , is soluble in water and alcohol, and crystallises from benzene in needles. Cryoscopic determinations of its molecular weight show that this corresponds with the simple formula  $C_3H_5O_3N$ . When dissolved in water, it reacts as a monobasic acid, and determinations of its electrical conductivity indicate that its strength is half that of acetic acid, the value of  $K$  for nitroacetone being 0.001026. Aminoacetone (Abstr., 1893, 734) is obtained by reducing nitroacetone, and this result indicates that the latter is a nitro-compound and not a nitrite. In aqueous solutions, both nitroacetophenone and nitroacetone behave like isonitroso-derivatives (Hantzsch and Veit, Abstr., 1899, i, 401), but the latter substance does not appear to have any close connection with the compound described as a nitroacetone by Henry (Abstr., 1899, i, 475). When treated with phenylhydrazine, nitroacetone yields an oily *phenylhydrazone*. G. T. M.

**$\gamma$ -Amino- $\beta\beta$ -dimethylbutane.** By WASSILY SOLOXINA (Chem. Centr., 1899, ii, 474; from J. Russ. Chem. Soc., 1899, 31, 541—542).— $\gamma$ -Amino- $\beta\beta$ -dimethylbutane, prepared by reducing a boiling alcoholic solution of pinacolone oxime,  $CMe_3 \cdot CMe \cdot NOH$ , with sodium, is a mobile liquid, has the odour of ammonia, boils at  $103$ — $104^{\circ}$ , and is very slightly soluble in water. At  $-20^{\circ}$ , it forms a crystalline mass. The *hydrochloride* forms long needles, and the *platinichloride* is crystalline; the *aurichloride* crystallises from dilute alcohol in long, pale yellow needles, and melts at  $178^{\circ}$ . By the action of benzenesulphonic chloride on aminodimethylbutane dissolved in ether, the compound  $C_6H_{13} \cdot NH \cdot SO_2Ph$  is formed which crystallises from aqueous alcohol



in thick plates, melts at  $96\cdot5^\circ$ , and is insoluble in water, but easily so in alcohol, ether, or benzene. E. W. W.

**$\beta$ -Heptylamine.** By THOMAS CLARKE (*J. Amer. Chem. Soc.*, 1899, 21, 1027—1031. Compare Cahours and Pelouse, *Jahresber.*, 1863, 528; Schorlemmer, *Annalen*, 1863, 127, 318).—When  $\beta$ -heptyl bromide (Abstr., 1881, 82) is heated with an excess of alcoholic ammonia at  $100^\circ$ , the products are primary  $\beta$ -heptylamine hydrobromide, heptylene, and ammonium bromide. The *hydrobromide*,



crystallises from a mixture of benzene and light petroleum in slender, silky needles melting at  $163^\circ$ , and dissolves readily in alcohol, water, or benzene, and also in large quantities of dry ether. The amine is a slightly brown liquid boiling at  $142\text{--}144^\circ$  under atmospheric pressure, and of sp. gr.  $0\cdot7667$  at  $24^\circ/24^\circ$ . It dissolves readily in alcohol, ether, or light petroleum, is extremely hygroscopic, and has strongly alkaline properties. The *hydrochloride* crystallises in colourless, silky, somewhat deliquescent needles melting at  $133^\circ$ ; the *platinichloride* crystallises from warm water in large, yellow plates decomposing at  $195^\circ$ ; the *aurichloride* also crystallises in large, yellow plates melting at  $63\text{--}64^\circ$ , and the *ovalate*,  $(\text{C}_7\text{H}_{17}\text{N})_2\cdot\text{H}_2\text{C}_2\text{O}_4$ , in colourless plates which melt and decompose at  $204\text{--}205^\circ$ , and also decompose when boiled with water. J. J. S.

**Behaviour of Diamines on Neutralisation.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 694—700).—The differences observed in the heats of neutralisation for successive equivalents of acid afford a method of distinguishing between monoacid and polyacid bases, and of fixing their molecular weight. The same end is more quickly attained by titrating the base with standard acid and observing the behaviour of different indicators; ethylenediamine and diethylenediamine are thus shown to be monoacid towards phenolphthalein, and diacid towards methyl-orange. Both these bases may be estimated alkalimetrically with considerable accuracy, but the end points are not so delicate with diethylenediamine as with ethylenediamine, a fact which is in harmony with the lower heat of neutralisation of the former base. N. L.

**Diamines. Diethylenediamine (Piperazine).** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 687—694).—Diethylenediamine hydrate,  $\text{C}_4\text{H}_{10}\text{N}_2 + 6\text{H}_2\text{O}$ , melts at  $44^\circ$ ; when distilled, a mixture of water and diethylenediamine passes over, the proportion of the latter gradually increasing as the temperature rises until, above  $135^\circ$ , the anhydrous base is obtained. This is a crystalline, tenacious, waxy substance which melts at  $104^\circ$  and dissolves very slowly in water, but is nevertheless very hygroscopic. The heat of dissolution of the base is  $+5\cdot16$  Cal. at  $14^\circ$ , and of the hydrate  $-9\cdot15$  Cal. at  $16^\circ$ . The heat of hydration is therefore  $+14\cdot31$  Cal. (liquid water) or  $4\cdot9$  Cal. (solid water). No evidence was found for the existence of more than one hydrate. The heat of combustion of diethylenediamine hydrate is  $691\cdot11$  Cal. at constant volume, and  $691\cdot3$  Cal. at constant pressure. The heat of formation of the base

from its elements is 16.6 Cal., and its heat of combustion is calculated as 705.6 Cal.

Comparison of the heat of formation of diethylenediamine with that of ethylenediamine (8.8 Cal.) shows that the conversion of the latter compound into the former, by the fixation of a  $C_2H_2$  group, is accompanied by the development of +7.8 Cal., whereas this transformation, instances of which are cited, is always accompanied by the absorption of heat when the general function of the compound remains unaltered. These facts are in harmony with the view that diethylene-diamine is a cyclic compound.

The heat of neutralisation of diethylenediamine is 10.36 Cal. for the first, and 7.05 Cal. for the second, equivalent of hydrochloric acid, all the substances being in solution; diethylenediamine is therefore a weaker base than ethylenediamine, the corresponding figures for which are 12.52 and 11.0 respectively. The heat of dissolution of the hydrated dihydrochloride,  $C_4H_{10}N_2 \cdot 2HCl + H_2O$ , is +6.0 Cal., and of the anhydrous salt, -4.09 Cal.; the heat of hydration is therefore +1.91 Cal. (liquid water) and +0.3 Cal. (solid water). The heat of formation of the solid anhydrous dihydrochloride from the solid base and the gaseous acid is +61.4 Cal. In the activity of its basic function, diethylene-diamine is inferior to ammonia, ethylamine, and methylamine, but superior to aniline.

N. L.

**Amic Acids and Imides of Aliphatic Dicarboxylic Acids.** By KARL AUWERS [FRITZ MAYER, and F. SCHLEICHER] (*Annalen*, 1899, 309, 316—347).—The author's method for identifying dicarboxylic acids of the aliphatic series (Abstr., 1895, i, 504) meets with certain difficulties (compare Abstr., 1896, i, 639, and 1898, i, 126) which are discussed in the present paper, particularly with regard to the structurally isomeric amic acids of monoalkylsuccinic acids,  $CO_2H \cdot CHR \cdot CH_2 \cdot CONHR$  and  $CONHR \cdot CHR \cdot CH_2 \cdot CO_2H$ , of *as*-dialkylsuccinic acids, and to those *s*-dialkylsuccinic acids which occur in two stereoisomeric forms. It is found that the imides obtained from the structurally isomeric amic acids of monoalkylsuccinic acids by heating them alone, or with acetyl chloride, are identical, and the same remark applies to the amic acids of *as*-dialkylsuccinic acids; when the imides are hydrolysed with alkali, the amic acids produced are either the original ones, their structural isomerides, or mixtures of the two. The following facts in connection with *s*-dialkylsuccinic acids have been ascertained: 1. The fumaroid acid is converted into the fumaroid imide by heating it with a base during a short period, or by heating the fumaroid anilic acid above its melting point; this does not apply to the anil, tolil, and  $\beta$ -naphthil of fumaroid diethylsuccinic acid, because these imides are very labile, and thus become converted into the corresponding maleoid derivatives. 2. Hot acetyl chloride converts the fumaroid anilic acids into the maleoid compounds. 3. Boiling dilute acids convert the fumaroid and maleoid imides into the corresponding fumaroid and maleoid dicarboxylic acids, with a small proportion of the stereoisomeric modifications. 4. Boiling, dilute, aqueous alkalis resolve the anils into the corresponding anilic acids. The *p*-tolil of maleoid

dimethylsuccinic acid yields the maleoid *p*-tolilic acid with aqueous caustic soda, and the fumaroid *p*-tolilic acid with baryta. 5. Alcoholic soda and potash also convert imides into amic acids, but at the same time change the fumaroid compound into the maleoid, the converse taking place to only a slight extent; in some cases, however, the rearrangement does not occur. 6. On the other hand, hot, concentrated aqueous alkalis invariably convert the maleoid amic acids into the fumaric modification; this action is not reversible.

The following melting points are recorded: Methylsuccinic acid *p*-tolilic acid,  $164^{\circ}$ , *p*-tolil,  $109-110^{\circ}$ ,  $\beta$ -naphthilic acid,  $154.5^{\circ}$ ,  $\beta$ -naphthil,  $160.5^{\circ}$ . Isopropylsuccinic acid anilic acid,  $143^{\circ}$ , anil,  $91-92^{\circ}$ , *p*-tolilic acid,  $143-144^{\circ}$ , *p*-tolil,  $139-140^{\circ}$ ,  $\beta$ -naphthilic acid,  $198^{\circ}$ ,  $\beta$ -naphthil,  $132-132.5^{\circ}$ . *as*-Dimethylsuccinic acid anilic acid,  $84-86^{\circ}$ , *p*-tolil,  $113^{\circ}$ . Fumaroid *s*-dimethylsuccinic acid *p*-tolilic acid,  $194^{\circ}$ , *p*-tolil,  $120-121^{\circ}$ ,  $\beta$ -naphthilic acid,  $209^{\circ}$ ; maleoid *s*-dimethylsuccinic acid *p*-tolilic acid,  $164^{\circ}$ , *p*-tolil,  $153^{\circ}$ ,  $\beta$ -naphthilic acid,  $140^{\circ}$ ,  $\beta$ -naphthil,  $220^{\circ}$ . Fumaroid *s*-methylethylsuccinic acid anilic acid,  $164-165^{\circ}$ , anil,  $76-77^{\circ}$ , *p*-tolilic acid,  $175^{\circ}$ , *p*-tolil,  $87-88.5^{\circ}$ ,  $\beta$ -naphthilic acid,  $191-192^{\circ}$ ,  $\beta$ -naphthil,  $148-150^{\circ}$ ; maleoid *s*-methylethylsuccinic acid anilic acids,  $139-140^{\circ}$ , and  $100-102^{\circ}$ , anil,  $103-104^{\circ}$ , *p*-tolilic acid,  $147-148^{\circ}$ , *p*-tolil  $109-110^{\circ}$ ,  $\beta$ -naphthil  $159-160^{\circ}$ . Fumaroid *s*-diethylsuccinic acid anilic acid,  $183-184^{\circ}$ , *p*-tolilic acid,  $189-190^{\circ}$ ,  $\beta$ -naphthilic acid,  $202-203^{\circ}$ , maleoid *s*-diethylsuccinic acid anilic acid,  $124-125^{\circ}$ , anil,  $84-85^{\circ}$ , *p*-tolilic acid,  $148-149^{\circ}$ , *p*-tolil,  $92-93^{\circ}$ ,  $\beta$ -naphthilic acid,  $145-146^{\circ}$ ,  $\beta$ -naphthil,  $118-119^{\circ}$ . *d*-Camphoranilic acid,  $203-204^{\circ}$ , *d*-camphoranil,  $117-118^{\circ}$ ; *l*-iso-camphoranilic acid,  $183-183.5^{\circ}$ . Succinic acid *p*-tolilic acid,  $179-180^{\circ}$ , *p*-tolylamide,  $207^{\circ}$  (compare Auwers and Harger, Abstr., 1896, i, 640); dibromosuccinanil,  $\begin{array}{c} \text{CHBr}\cdot\text{CO} \\ | \\ \text{CHBr}\cdot\text{CO} \end{array} \text{>NPh}$ , prepared from bromine and the anil of maleic acid,  $171^{\circ}$  (compare Auwers and Singhof, Abstr., 1896, i, 644), chlorosuccinanil,  $\begin{array}{c} \text{CH}_2\text{--CO} \\ | \\ \text{CHCl}\cdot\text{CO} \end{array} \text{>NPh}$ ,  $117-118^{\circ}$ .

M. O. F.

**Methyleneasparagine and Allied Compounds.** By HUGO SCHIFF (*Gazzetta*, 1899, 29, ii, 285-303. Compare Abstr., 1899, i, 870).—When exposed to the air, dimethyleneasparagine gives up formaldehyde, the residual substance having a composition corresponding to a *sesquimethyleneasparagine*,  $\text{CH}_2(\text{C}_4\text{H}_5\text{O}_3\text{N}_2\text{CH}_2)_2$ ; its copper compound has the composition  $\text{C}_{11}\text{H}_{11}\text{O}_6\text{N}_4\text{Cu} + \text{H}_2\text{O}$ .

Methyleneasparagine acts as a monobasic acid; at  $14^{\circ}$ , it dissolves in water to the extent of 2.38 per cent., but it is scarcely soluble in alcohol. On allowing its solution in alcoholic hydrochloric acid to evaporate over sulphuric acid, it deposits colourless needles of the hydrochloride of monoethyl aspartate. In aqueous solution,  $[a]_D$  has a mean value  $-47.58^{\circ}$ ; a solution containing methyleneasparagine and potassium hydroxide in molecular proportion gives for potassium methyleneasparaginate  $[a]_D - 69.01^{\circ}$ . The presence of a large quantity of water hinders the formation of methyleneasparagine;

on diluting a solution of methyleneasparagine, however, it is not decomposed.

A solution of  $\alpha$ -asparagine required for neutralisation 0.63 mol. of potash per mol. of the asparagine, whilst after adding formaldehyde the quantity of potash necessary was increased to 0.95 mol.

The author prefers Piutti's formula,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CMe}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , for homoasparagine, since it resembles  $\beta$ -asparagine in having a feeble acid reaction and in giving an azure-violet biuret reaction.

*Methylenhomoasparagine*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CMe}(\text{N}:\text{CH}_2) \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$ , is a colourless, crystalline compound which dissolves readily in water, but only slightly in alcohol, and does not give the biuret reaction. It behaves as a monobasic acid and forms a copper compound,  $(\text{C}_6\text{H}_9\text{O}_3\text{N}_2)_2\text{Cu}$ .

Methyl- $\alpha$ -asparagine gives a reddish-violet biuret reaction, but if formaldehyde is present, no coloration is obtained; it acts as a monobasic acid. Dimethyl- $\alpha$ -asparagine, however, has much feebler acid properties; a concentrated solution neutralises 0.2 mol. of potash per mol. The addition of formaldehyde makes the solution strongly acid again, so that a further 0.6 mol. of potash is required for neutralisation; in the course of an hour, further addition of 0.2 mol. of potash is necessary, the total amount of potash added being 1 mol. for each mol. of the dimethylasparagine. A solution of 1 mol. of dimethylasparagine in 1320 mols. of water, is, however, neutral, but on adding formaldehyde neutralises at once 0.6 mol. of potash, and in the course of the day the remaining 0.4 mol. must be added to keep the solution neutral.

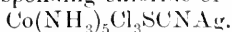
In concentrated aqueous solution, 1 mol. of glutamine neutralises 0.1 to 0.15 mol. of potash; on adding formaldehyde, methyleneglutamine is formed, and acts as a monobasic acid, neutralising a molecular proportion of potash. *Methyleneglutamine* is a colourless, crystalline mass which dissolves readily in water and decomposes carbonates; with copper hydroxide, it forms a dark azure-blue compound apparently very soluble in water.

T. H. P.

Nitrosoalkylurethanes. By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3148—3149).—A reply to Brühl (*Abstr.*, 1899, i, 871). T. M. L.

Constitution of Inorganic Compounds. XX. Thiocyanocobalt Salts and Structural Isomerides. By ALFRED WERNER, HERBERT MÜLLER, R. KLIEN, and F. BRÄUNLICH (*Zeit. anorg. Chem.*, 1899, 22, 91—157).—*Isothiocyanopentammine salts*,  $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{X}_2$ , are obtained by the action of potassium thiocyanate on concentrated hot solutions of aquopentammine salts, the sulphate being most advantageously employed; blackish-green additive products of thiocyanic acid and the isothiocyano-salt are formed, but are decomposed on addition of water. The thiocyano-group in these compounds is not dissociated even in dilute aqueous solution, and the characteristic reaction with ferric chloride does not take place. The thiocyano-group is also unaltered by the action of mineral acids, whereby the other acid groups undergo substitution. With silver nitrate, additive compounds of the formula  $\text{Co}(\text{NH}_3)_5(\text{NO}_3)_2\text{SCNAg}$  are formed, which, when treated with

hydrochloric acid, do not give a precipitate of silver chloride, but are converted into the corresponding chloride of the formula



*Isothiocyanopentamminecobalt sulphate*,  $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{SO}_4 + 2\text{H}_2\text{O}$ , crystallises in four-sided, thin, yellow plates, and is converted into the hexammine chloride when oxidised with chlorine. The *nitrate*, *chloride*, *bromide*, *iodide*, *platinichloride*, *platinosochloride*, *thiocyanate*, and *nitrite*, obtained by treating the sulphate with the corresponding acids, are also described.

*Nitritothiocyanotetramminesalts*,  $[\text{CoNO}_2(\text{NH}_3)_4\text{SCN}]\text{X}$ .—The *chloride* is obtained by the action of potassium thiocyanate on a hot solution of chloronitritotetramminecobalt chloride and subsequent treatment with hydrochloric acid. The thiocyanato-group in these compounds is not so firmly combined as in the preceding series, and is gradually completely dissociated in dilute solution; with silver nitrate, similar additive products of the formula  $[\text{CoNO}_2(\text{NH}_3)_4\text{SCNAg}]\text{ClNO}_3$  are obtained, which, however, when boiled with water, are decomposed into silver chloride and nitritothiocyanotetramminecobalt nitrate; when shaken with silver oxide, the corresponding base is not obtained, but decomposition takes place with the formation of silver chloride and thiocyanate and the base of the nitritoquotetrammine series. *Nitritothiocyanotetramminecobalt chloride* crystallises in lustrous leaflets when precipitated from aqueous solution by hydrochloric acid, and in needles and tabular prisms from neutral aqueous solution, is soluble in 33 parts of water, and when oxidised with chlorine yields chloronitritotetraammine chloride. The *bromide*, *iodide*, *thiocyanate*, and *nitrate* are also described.

*Dithiocyanodiethylenediaminecobalt salts*,  $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SCN})_2]\text{X}$ .—By the action of potassium thiocyanate on dichlorodiethylenediaminecobalt chloride and subsequent evaporation with hydrochloric acid, the chlorides of two isomeric dithiocyanodiethylenediaminecobalt salts are obtained. This isomerism is determined by the isomerism of the dichlorodiethylenediamine salts, since the 1:2-dichlorodiethylenediamine salts (violeo-salts) yield only one dithiocyano-series, the easily soluble salts containing *iso*-thiocyano-groups, whereas 1:6-dichlorodiethylenediamine salts (praseo-series) yield both series of salts and more of the sparingly soluble series, containing thiocyano-groups, as the concentration of the solution to which the potassium thiocyanate is added increases. The easily soluble dithiocyanochloride, when oxidised with chlorine, is converted into diamminediethylenediaminecobalt chloride, that is, the nitrogen atom of the thiocyano-group in direct combination with the cobalt atom is converted into ammonia. The sparingly soluble isomeric chloride, however, when oxidised with chlorine, yields dichlorodiethylenediaminecobalt chloride, in which the thiocyano-group is completely oxidised. As regards the thiocyano-groups, the isomerism is evidently similar to that between the thio-carbimides and the thiocyano-esters. *Diisothiocyanodiethylenediaminecobalt chloride* crystallises, with  $11\text{H}_2\text{O}$ , in thin, triclinic, ruby-red tablets of rhomboidal habit, and, with  $1\frac{1}{2}\text{H}_2\text{O}$ , in thick, rhomboidal tablets which appear black in reflected light, is easily soluble in cold water,

yielding a bright ruby-red solution. The *thiocyanate*, *hydrogen sulphate*, *nitrate*, *bromide*, and *iodide* are also described. A normal sulphate cannot be prepared, and this forms a marked distinction between this series and the sparingly soluble series from which only the normal sulphate is obtained.

*Dithiocyanodiethylenediaminecobalt chloride* crystallises, with  $\text{H}_2\text{O}$ , in thin, yellowish-red needles or prisms having a bronze lustre, and in flat, rhomboidal prisms which appear almost black in reflected light, is practically insoluble in cold water, fairly soluble in hot water, and gives a yellowish-red solution. The *thiocyanate*, *sulphate*, *nitrate*, *bromide*, and *iodide* are also described.

*Diamminediethylenediaminecobalt chloride*,  $[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{H}_8\text{N}_2)_2]\text{Cl}_2 + \text{H}_2\text{O}$ , obtained by oxidising the above diisothiocyanochloride with chlorine, crystallises in triclinic, many-sided tablets, and in four-sided, yellow pyramids. The aqueous solution is completely precipitated by alcohol, and gives the typical luteo-salt reactions. With cobaltous chloride, similarly to the triethylenediaminecobalt chloride, it yields a *double salt* which crystallises, with  $2\text{H}_2\text{O}$ , in thin, four-sided plates.

The thiocyno-group is generally combined in the normal manner. In the four series of compounds, thiocyanopentammine salts, nitrothiocyanotetrammine salts, chlorothiocyanodiethylenediamine salts, and oxalothiocyanotriammine salts, only the first series are derivatives of isocyanic acid, since, when oxidised with chlorine, they yield hexammine salts. The remaining salts, when oxidised with chlorine, yield respectively chloronitritotetrammine salts, trichlorodiethylenediamine salts, and oxaloaquotriammine salts. Further, the thiocyno-residues in Reinecke's salt,  $\text{Cr}(\text{NH}_3)_2(\text{SCN})_4\text{K}$ , and in potassium platinithiocyanate, are completely oxidised and eliminated by chlorine.

The conversion of isothiocyno-group into the ammonia group which remains in direct combination with the cobalt atom, shows that the ammonia molecules in the complex radicle are combined with the metal atom in the same manner as acid groups which are in direct combination with the metal atom. The direct substitution of ammonia by acid groups and the converse substitution cannot be effected, as a rule, in the cobaltammonia compounds. When, however, chloroamminediethylenediaminecobalt chloride is treated with potassium thiocyanate, the ammonia group is replaced by the thiocyno-group, and chlorothiocyanodiethylenediaminecobalt thiocyanate is formed.

*Dichlorodiethylenediaminecobalt thiocyanate*,  $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)\text{Cl}_2]\text{CNS}$ , obtained by adding potassium thiocyanate to an aqueous solution of the diethylenediaminepraseo-chloride, crystallises in small, lustrous, green, six-sided prisms.

*Chlorothiocyanodiethylenediaminecobalt thiocyanate*,  $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)\text{Cl}\cdot\text{SCN}]\text{SCN}$ , obtained by boiling dichlorodiethylenediaminecobalt chloride with potassium thiocyanate, is a brownish-violet, crystalline powder which, when heated with water, decomposes into the isomeric dithiocyanochlorides, and when evaporated with hydrochloric acid yields the salt  $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)\text{ClSCN}]\text{Cl}$ .  
E. C. R.

**Organo-mercuric Compounds.** By GEORGES DENIGÈS (*Ann. Chim. Phys.*, 1899, [vii], 18, 382—432. Compare Abstr., 1895, i, 411; 1898, i, 546, 549, 618; 1899, i, 22, 414, ii, 256).—Citric acid, even when in dilute solution, is readily oxidised by potassium permanganate to acetonedicarboxylic acid; the latter combines readily with mercuric sulphate, forming an insoluble compound (Abstr., 1899, ii, 454); this reaction may be utilised in detecting small quantities of the former acid in the juices of plants, wines, milk, &c. Glycerol, gum, dextrose, sucrose, and acetic, tartaric, malic, succinic, and lactic acids do not interfere with the reaction, but oxalic acid must be removed either by a preliminary oxidation with excess of permanganate or by precipitation as mercuric oxalate.

G. T. M.

**Tungsten Alkyls.** By EDGAR F. SMITH, E. A. BARNETT, and CLARENCE HALL (*J. Amer. Chem. Soc.*, 1899, 21, 1013—1016).—It has not been found possible to obtain the compound,  $\text{WMe}_3\text{I}$ , described by Riche (*Compt. rend.*, 1856, 42, 203) and by Cahours (*Annalen*, 1862, 122, 70); the authors obtained a black substance, containing over 94 per cent. of tungsten, together with small quantities of carbon and iodine. No tungsten alkyl is obtained when tungsten hexachloride is treated with mercuric ethyl or zinc methyl, nor yet by the action of methyl iodide on tungsten prepared by various methods.

J. J. S.

**Cyclic Compounds, Ethylhexanaphthene and Mercuro-heptanaphthene Iodide.** By N. KURSNOFF (*Chem. Centr.*, 1899, ii, 477; from *J. Russ. Chem. Soc.*, 1899, 31, 534—535).—By the action of zinc ethyl on chloro- or iodo-naphthene, about 30 per cent. of *ethyl-naphthene* is obtained; it boils at 132—133° and has a sp. gr. 0.7913 at 0°/0° and 0.7772 at 20°/0°. A vapour density determination gave 4.04. Naphthylene (cyclohexene), ethylene, ethane, and saturated condensation products boiling at 242—243° under 755 mm. pressure are also formed.

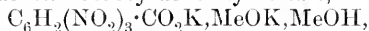
“Mercuro-heptanaphthene iodide,”  $\text{C}_6\text{H}_{11}\text{HgI}$ , prepared by the action of sodium amalgam on iodo-hexamethylene, crystallises from hot alcohol in lustrous, white scales, melts at 142°, and is decomposed by prolonged heating with liberation of mercuric iodide. E. W. W.

**Derivatives of Nitroic Acids. Reactions of Nitro-compounds.** By ARTHUR HANTZSCH and HERMANN KISSEL (*Ber.*, 1899, 32, 3137—3148. Compare Abstr., 1899, i, 404).—The names ‘*nitroic acid*’ and ‘*nitroic ester-acid*’ are given to the acids  $\text{R}\cdot\text{NO}(\text{OH})_2$  and  $\text{R}\cdot\text{NO}(\text{OR}')\cdot\text{OH}$ , formed by the addition of water and alcohols to certain nitro-compounds.

*Trinitrotoluene potassium methoxide* (potassium methyl dinitrotoluene-nitroate),  $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2\cdot\text{NO}(\text{OMe})\cdot\text{OK} + \text{H}_2\text{O}$ , is a dark violet salt, which explodes when heated;  $\mu_{61}$  96.0 and  $\mu_{1021}$  113.0, at 25°, showing that the salt is hydrolysed to a considerable extent. The ester-acid, *hydrogen methyl dinitrotoluenenitroate*, is a dark red substance which dissolves only slightly in water or in organic solvents, except acetic acid, in which it has a normal molecular weight; it is a

feeble acid,  $\mu_{1024}$  15 at  $25^\circ$ , and is stable in aqueous solution, but evolves nitrous acid when boiled with dilute acids, and gives trinitrotoluene and methyl alcohol when dissolved in concentrated sulphuric acid; it is not attacked by phosphorus pentachloride, and crystallises unchanged from acetic acid, but acetyl chloride converts it into *acetyl methyl dinitrotoluenenitroate*, a microcrystalline substance which explodes on gentle warming, and is hydrolysed by alkalis.

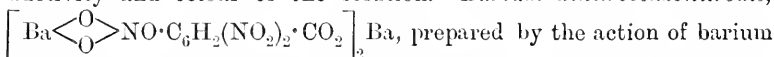
Potassium methyl dinitrobenzenenitroate (trinitrobenzene potassium methoxide) and *potassium methyl dinitroxylenenitroate* (*trinitroxylene potassium methoxide*) are immediately decolorised by acids, and do not give nitroic ester-acids. Lobry de Bruyn's salt,



gives an unstable *nitroic ester-acid*, from which trinitrobenzoic acid is regenerated on evaporating the solution.

*p*-Nitrobenzylnitramine (Hantzsch and Hilland, *Ber.*, 31, 2058) interacts with 2 mols. sodium ethoxide to form the *sodium ethyl nitroate*,  $\text{N}_2\text{O}_2\text{Na} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}(\text{OEt}) \cdot \text{ONa}$ , a deep-red, soluble salt which decomposes in moist air, cannot be recrystallised, and sometimes inflames spontaneously in the desiccator. The *ester-acid* is also extremely unstable, and changes quickly into a yellow resin, from which *p*-nitrobenzoic acid was obtained.

Sodium trinitrobenzoate combines, at least partially, in solution with another molecule of sodium hydroxide to form a *sodium nitroate*, which could not be isolated, but was shown to be present by the conductivity and colour of the solution. *Barium dinitrobenzonitroate*,



hydroxide on trinitrobenzoic acid, is a dark, brownish-red salt, very slightly soluble in water, and very explosive; the nitroic acid is unstable. Trinitrobenzene and trinitrotoluene dissolve in caustic alkalis, giving deep red solutions, but the formation of nitroates appears to be only very partial; on acidifying the alkaline solutions at  $6^\circ$ , red solutions are obtained which appear to contain the nitroic acids, but these are unstable at the ordinary temperature.

Hepp's trinitrobenzene potassium cyanide (*Annalen*, 1883, 215, 360), to which the formula  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NO}(\text{CN}) \cdot \text{OK}$  is assigned, is a deep-violet, crystalline, explosive salt; *dinitrobenzenecyanonitroic acid* (*trinitrobenzene cyanhydrin*), which is precipitated by mineral acids from a solution of the potassium salt, crystallises from ether or benzene in red needles, and decomposes at  $175^\circ$ ; it is not acted on by phosphorus pentachloride or acetyl chloride.

The characteristic reactions of the nitro-paraffins are shown to be really those of the isonitro-compounds. Nitroethane is scarcely attacked by bromine in aqueous solution, but a solution of isonitroethane, freshly prepared at  $0^\circ$  by the action of hydrochloric acid on the sodium salt, brominates completely and smoothly. A solution of nitroethane gives no nitrolic acid with nitrous acid, but isonitroethane interacts readily with it. Isonitroethane and diazonium hydroxide interact immediately at  $0^\circ$ , whilst true nitroethane is inactive; similarly, phenylisonitromethane interacts readily with diazonium hydroxide and isonitroethane with *p*-bromodiazonium hydroxide. The conclu-



sion is drawn that the true nitro-compounds are, of themselves, no more active than the corresponding halogen compounds, and owe their apparent chemical activity entirely to the formation of the labile isonitro-compounds, and not to the negative character of the  $-\text{NO}_2$  group. T. M. L.

**Transformation of Styrene into Metastyrene under the Influence of Light.** By GEORGES LEMOINE (*Compt. rend.*, 1899, 129, 719—722. Compare Abstr., 1898, i, 70).—The polymerisation of styrene is effected by the action of heat in the dark, and also under the influence of sunlight at the ordinary temperature; in the latter case, the action is slower, 1—3 per cent. of the substance being transformed in an hour. In this change, the blue and ultra-violet rays are principally concerned; their activity does not extend much below a depth of 4 mm., and is greatly decreased by cooling the insulated liquid; the action does not continue after removal from the influence of light, or only to a very small extent. The velocity of transformation in the light is approximately equal to that observed in the dark at a temperature 50° higher. The general conclusion arrived at is that, in the conversion of styrene into metastyrene, light exerts an accelerating action on an exothermic transformation which takes place in the dark at the same temperature, although more slowly.

N. L.

**Naphthalene-1:3:5-trisulphonic Acid.** By HUGO ERDMANN (*Ber.*, 1899, 32, 3186—3191. Compare Armstrong and Wynne, *Proc.*, 1887, 146, and 1893, 166).—Polysulphonic acids containing two or three sulphonic groups in  $\beta$ -positions are obtained when naphthalene is sulphonated with fuming sulphuric acid at high temperatures; of these, the 1:3:6-trisulphonic acid, recognised by its sodium and lead salts and its chloride, is the chief product (*Proc.*, 1887, 146).

Naphthalene-1:3:5-trisulphonic acid, the original product of sulphonation, is only obtained when the whole of the reaction is carried out below 90°. Sodium naphthalene-1:5-disulphonate is mixed with fuming sulphuric acid at 50°, and the reaction completed at 90°; the 1:3:5-acid which is thus produced is separated in the form of its sodium salt; this compound is converted into the sulphonic chloride (m. p. 145—148°), which is then boiled with methyl alcohol, and the solution evaporated to dryness; in this way, the acid is obtained as a colourless syrup.

Naphthalene-1:3:5-trisulphonic acid resembles the non-volatile mineral acids; it is very hygroscopic, destroys cellulose with liberation of carbon, and decomposes sodium chloride.

The *aniline* salt,  $\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_3 \cdot 3\text{NH}_2\text{Ph}$ , produced by adding aniline to an aqueous solution of the acid, or by double decomposition from aniline hydrochloride and sodium naphthalenetrisulphonate, crystallises from water in aggregates of white, silky needles. The salt is not hygroscopic, and is readily soluble in water, but less so in brine solution. The *p-toluidine* salt is more soluble than the aniline compound; the *benzidine* salt,  $2\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_3 \cdot 3\text{C}_6\text{H}_4(\text{NH}_2)_2$ , crystal-

lises with  $4\text{H}_2\text{O}$ , and the dianisidine salt separates slowly from its solution in glacial acetic acid in short, hard needles. G. T. M.

**Polymerisation of Inorganic Chloroanhydrides. II.** By GIUSEPPE ODDO (*Gazzetta*, 1899, 29, ii, 330—343. Compare also this vol., ii, 74).—The products obtained on heating phosphorus pentachloride and oxychloride, in a reflux apparatus, with varying quantities of water are as follows: With  $2\text{PCl}_5 + \text{H}_2\text{O}$ , half of the pentachloride is converted into oxychloride, the rest being unchanged;  $2\text{PCl}_5 + 2\text{H}_2\text{O}$  yields the theoretical amount of oxychloride;  $2\text{PCl}_5 + 3\text{H}_2\text{O}$  or  $(\text{POCl}_3)_2 + \text{H}_2\text{O}$  gives mainly oxychloride accompanied by a little pyrophosphoryl chloride,  $\text{P}_2\text{O}_3\text{Cl}_4$ , and phosphoric oxide; with the proportions  $2\text{PCl}_5 + 4\text{H}_2\text{O}$  or  $(\text{POCl}_3)_2 + 2\text{H}_2\text{O}$ , the same products as in the previous case are obtained, the amount of oxychloride being considerably diminished, and that of phosphoric oxide correspondingly increased.

The interaction of phosphorus pentachloride (3 mols.) on phosphoric oxide (1 mol.), yields a little oxychloride and a considerable quantity of pyrophosphoryl chloride, and is recommended as a good method for preparing the latter.

Potassium chlorate reacts with phosphorus oxychloride according to the equation  $(\text{POCl}_3)_2 + \text{KClO}_3 = \text{P}_2\text{O}_5 + \text{KCl} + 3\text{Cl}_2$ . This reaction offers a convenient method of chlorination where a definite quantity of chlorine is required.

By heating together phosphorus oxychloride and aniline hydrochloride in molecular proportions in a reflux apparatus, hydrogen chloride is evolved and dichlorophosphoxymonoanilide,  $\text{NHPh}\cdot\text{POCl}_2$ , obtained. The molecular weight of the latter in boiling benzene varies from 215 with a concentration 0.7944 to 276 when the concentration is 5.2183; using the same solvent, the numbers given by the cryoscopic method are 221 (concentration 0.9676) and 252 (concentration 1.8323). The calculated value is 210. Michaelis and Schulze (*Abstr.*, 1894, i, 128) state that this compound distils in a vacuum with partial decomposition; the author finds, however, that at  $90^\circ$  evolution of hydrogen chloride commences, and at  $180^\circ$  continues until 1 mol.  $\text{HCl}$  is lost per molecule of the substance, the residue being a new compound to be described later.

Using three mols. of aniline hydrochloride to one of phosphorus oxychloride, two products are obtained. The first, monochlorophosphoxydianilide,  $\text{POCl}(\text{PhNH})_2$ , gives, in boiling alcohol, a molecular weight varying from 270 with a concentration of 1.3856 to 184 when the concentration is 3.6192; the molecular weight falls if the boiling be prolonged. These observations are at variance with those of Michaelis and Schulze (*Abstr.*, 1894, i, 588). The other product is oxyphosphoazobenzeneanilide, melting at  $320\text{--}325^\circ$ , and not at  $357^\circ$  as stated by Michaelis and Silberstein (*Abstr.*, 1896, i, 344).

If six molecular proportions of a benzene solution of aniline be treated with one of phosphorus oxychloride, the trianilide of orthophosphoric acid,  $\text{PO}(\text{PhNH})_3$ , is obtained; its molecular weight in boiling alcohol is 358—359, the calculated value being 323.

The action of phosphorus oxychloride on phenol yields the compound  $\text{POCl}_2 \cdot \text{OPh}$ , which gives the normal molecular weight in boiling benzene, a little of the chloride  $\text{POCl}(\text{OPh})_2$ , triphenyl phosphate, which in boiling benzene has the normal molecular weight, and a little diphenylphosphinic acid.  
T. H. P.

**Salicylanilinoacetic Acid** [*o*-Carboxyphenylglycollic Acid Monanilide] and its Derivatives. By GEORG COHN (*J. pr. Chem.*, 1899, [ii], 60, 404—406).—The *monoanilide* of *o*-carboxyphenylglycollic acid,  $\text{NHPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared by the action of chloroacetic acid on salicylaniline, separates from alcohol, in which it is readily soluble, in white needles melting at  $159^\circ$ .

The corresponding *phenetidide* crystallises from methyl alcohol, in which it is sparingly soluble, in rhombic leaflets melting at  $175$ — $178^\circ$ .

The *anisidine* compound,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises from methyl alcohol in bundles of long needles and melts indefinitely at  $174^\circ$ .  
A. L.

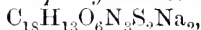
**Diphenylamine Derivatives, especially Sulphonic Acids.** By ROBERT GNEHM and H. WERDENBERG (*Zeit. angew. Chem.*, 1899, 1027—1030, 1051—1055, and 1128. Compare Merz and Weith, this Journ., 1873, 74).—Sulphuric acid of  $66^\circ$  B $\acute{e}$ . does not react with diphenylamine in the cold, and even on warming at  $100$ — $150^\circ$  the chief sulphonation product is the disulphonic acid, although a considerable quantity of the base remains unaltered; the chief and, in some cases, the only product formed when concentrated sulphuric acid is employed, at temperatures between  $105^\circ$  and  $140^\circ$ , is the disulphonic acid. Fuming sulphuric acid of different strengths at  $50^\circ$  yields a mixture of mono- and di-sulphonic acids which it is impossible to separate. In all the experiments made, the unaltered diphenylamine was found to contain a substance soluble in ether and melting at  $246$ — $248^\circ$ .

Diphenylaminesulphonic acid is most readily obtained by sulphonating acetyldiphenylamine with fuming sulphuric acid (10—25 per cent. anhydride) and subsequently hydrolysing. In the sulphonation, it is advisable to add phosphoric oxide in order to hinder hydrolysis by the water formed.

*Barium acetyldiphenylamine sulphonate*,  $\text{C}_{28}\text{H}_{24}\text{O}_8\text{N}_2\text{S}_2\text{Ba}$ , is extremely hygroscopic, and could not be obtained in a crystalline condition. For the preparation of diphenylaminesulphonic acid, it is not necessary to isolate the pure acetyl derivative; the crude sulphonic mixture may be boiled with water for some 3 hours and then treated with barium carbonate. *Barium diphenylaminesulphonate*,  $\text{C}_{24}\text{H}_{20}\text{O}_6\text{N}_2\text{S}_2\text{Ba}$ , is very sparingly soluble in cold water, and crystallises in snow-white, anhydrous, glistening plates which do not decompose at  $170^\circ$ . The *copper* salt, with  $2\text{H}_2\text{O}$ , and the *sodium* salt were also prepared. Diphenylaminesulphonic acid condenses with formaldehyde in aqueous solution, yielding *trianilinotriphenylmethane-sulphonic acid*,  $\text{C}_{19}\text{H}_{31}\text{O}_6\text{N}_3\text{S}_2$ , which dissolves in water or alcohol, readily undergoes oxidation in solution, and turns pale blue on exposure to the air.

Diphenylaminesulphonic acid is best prepared from the copper salt ; it crystallises in colourless plates, is readily soluble in alcohol or water, and condenses with diazonium solutions, yielding acid dyes.

*Sodium p-sulphobenzeneazodiphenylaminesulphonate,*



crystallises from hot water in violet plates and dyes silk or wool orange-yellow. *Sodium hydroxydinitrobenzeneazodiphenylaminesulphonate*,  $\text{C}_{18}\text{H}_{12}\text{O}_8\text{N}_3\text{SNa}$ , forms glistening, brown plates. Diphenylaminesulphonic acid (2 mols.) forms a salt with picramic acid (1 mol.).

*Acetyldi-p-nitrodiphenylamine*,  $\text{NAc}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , obtained when acetyldiphenylamine is treated with a mixture of sulphuric and nitric acids at  $8-15^\circ$ , crystallises from hot alcohol in pale yellow, glistening plates melting at  $164^\circ$  and readily soluble in most organic solvents ; when warmed with concentrated hydrochloric acid, it yields di-*p*-nitrodiphenylamine.

When barium acetyldiphenylaminesulphonate is nitrated with a mixture of fuming sulphuric (5 per cent. anhydride) and fuming nitric acids, first at  $15^\circ$  and then at  $30-35^\circ$ , a nitro-derivative is formed the barium salt of which could not be obtained in a crystalline condition, but when hydrolysed with sulphuric acid (37 per cent.), *nitrodiphenylaminesulphonic acid* was obtained, the *barium* salt of which is readily soluble in water and forms dark red crystals. The acid has not been obtained in a pure form and is probably a mixture of ortho- and para-nitro-compounds.

Barium diphenylaminesulphonate is much more readily nitrated than its acetyl derivative, the most suitable reagent being a mixture of concentrated nitric and sulphuric acids at  $0^\circ$ . The product is a *mononitro*-derivative.

*Barium diphenylaminedisulphonate* separates from water in crystalline masses containing  $2\text{H}_2\text{O}$  ; the *potassium* salt contains  $1\frac{1}{2}\text{H}_2\text{O}$  and the *copper* salt  $4\text{H}_2\text{O}$  ; the *acid* is readily soluble in water or alcohol, and has only been obtained in the form of a syrup. When the barium salt is nitrated with a mixture of nitric acid of sp. gr. 1.4 and concentrated sulphuric acid, the product is a *mononitro*-derivative, the *barium* salt of which,  $\text{C}_{12}\text{H}_8\text{O}_8\text{N}_2\text{S}_2\text{Ba} + 2\text{H}_2\text{O}$ , forms indefinite, orange-red crystals readily soluble in warm water ; the *potassium* salt contains  $1\frac{1}{2}\text{H}_2\text{O}$ . When reduced by Claisen's method (*Ber.*, 1879, 12, 1946), *aminodiphenylaminedisulphonic acid* is obtained, the *barium* salt of which,  $\text{C}_{12}\text{H}_{10}\text{O}_6\text{N}_2\text{S}_2\text{Ba}$ , forms a reddish-coloured mass, readily soluble in water, but insoluble in alcohol.

J. J. S.

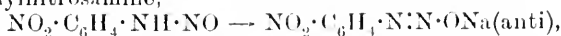
**Characterisation of Weak Acids and Pseudo-acids.** By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3066—3088. Compare Abstr., 1899, i, 399).—It is well known that the molecular conductivity,  $\mu$ , of the sodium salt of a comparatively strong acid increases with the dilution, and that the increase consequent on a doubling of the dilution has a diminishing value, tending towards 0 ; further, that the increase consequent upon a change of dilution from 32 to 1024 litres per gram-mol. ( $\Delta_{1024-32}$ ) has a value of 10—12 ; also, the sodium salts of such acids are neutral to litmus (or to a solution of potassium iodide and iodate), and are not hydrolysed appreciably in aqueous solu-

tion. Strong acids, moreover, combine with dry ammonia, both directly and when dissolved in non-dissociating media, such as benzene. In the case of very weak acids, the sodium salts are more or less hydrolysed; a certain amount of sodium hydroxide is present in the aqueous solution, which then has an alkaline reaction to litmus, and exhibits an increasing, instead of a decreasing, rate of increase of conductivity with dilution, and a resulting abnormally high value of  $\Delta_{1024-32}$  (regard must be had to the fact that the alkalinity may be due, as in the case of diazotates, to a little alkali from which it is practically impossible to free the salt). These regularities were investigated in the case of some weak, or very weak, acids, and the results are tabulated below:  $K$  is the value of the dissociation constant of the acid; and the percentage of the sodium salt hydrolysed in an aqueous solution containing 1 gram-mol. in 32 litres ( $V_{32}$ ) was determined approximately by measuring the hydrolysing effect upon methyl acetate (compare Shields, Abstr., 1893, ii, 448):

		Sodium salt. Per cent. hydro- lysed ( $V_{32}$ ).
	$K$ at 25°.	$\Delta_{1024-32}$
Phenol .....	$5 \times 10^{-7}$	28.0
<i>o</i> -Chlorophenol .....	—	16.7
2:4-Dichlorophenol .....	31 „	11.9
<i>p</i> -Cyanophenol ... ..	61 „	11.7
2:4:6-Trichlorophenol...	1000 „	—
<i>p</i> -Nitrophenol .....	96 „	11.9
		0.6
		2.1
		0.52
		0.52
		0.37
		0.28

It is noticeable that, although nitrophenol,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , is 10 times as weak an acid as trichlorophenol, yet its sodium salt is less hydrolysed; this salt must therefore be derived from an acid stronger than trichlorophenol, such as  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO} \cdot \text{OH}$ , and nitrophenol must be regarded in consequence as a pseudo-acid.

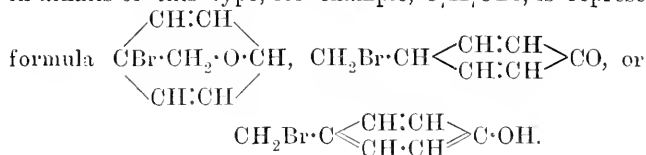
The following rules are given for use in the diagnosis of pseudo-acids. I. *The substance is neutral.* (1) The salt is neutral (therefore not hydrolysed, and so the salt of a strong acid): the substance is a pseudo-acid; for instance, phenylnitromethane,  $\text{CH}_2\text{Ph} \cdot \text{NO}_2 \rightarrow \text{CHPh} \cdot \text{NO} \cdot \text{ONa}$ . (2) The salt is alkaline: if  $\Delta_{1024-32}$  is not greater than 12—13 (or if the hydrolysis is small): the substance is a pseudo-acid; for instance, quinonehydrazone,  $\text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \rightarrow \text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{ONa}$ , and isonitrosoacetone,  $\text{NOH} \cdot \text{CH} \cdot \text{CMeO} \rightarrow \text{NO} \cdot \text{CH} \cdot \text{CMe} \cdot \text{ONa} (?)$ . II. *The substance is feebly, or very feebly acid.* (1) The salt is neutral: the substance is a pseudo-acid; for instance, nitrophenylnitrosamine,



ethylnitrolic acid,  $\text{CMe} \leq \text{NO}_2 \rightarrow \text{CMe} \leq \text{N} \xrightarrow{\text{NO}(\text{ONa})} \text{O}$ , and dinitroethane,  $\text{NO}_2 \cdot \text{CHMe} \cdot \text{NO}_2 \rightarrow \text{NO}_2 \cdot \text{CMe} \cdot \text{NO} \cdot \text{ONa}$ . (2) The salt is alkaline: if  $\Delta_{1021-32}$  is but slightly greater than the normal value, the substance is a pseudo-acid; for instance, *p*-bromophenylnitrosamine,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{NH} \cdot \text{NO} \rightarrow \text{C}_6\text{H}_4\text{Br} \cdot \text{N} \cdot \text{N} \cdot \text{ONa}$ ; if  $\Delta_{1021-32}$  is decidedly greater than the normal value, the percentage of hydrolysis must be determined: if this is much less than that of sodium

phenoxide, the substance is a pseudo-acid; in the opposite case, nothing can be predicated, and other properties must be taken into account. III. *The substance is a pronounced acid* with a dissociation constant readily susceptible of measurement; the salt is not perceptibly hydrolysed: the substance, at any rate the ionised part of it, has the same constitution as the ionised salt; it is possible that the undissociated substance may have a different constitution, when the case would be one of 'ionisation isomerism.' C. F. B.

**Bromophenols Insoluble in Alkalis.** By KARL AUWERS (*Ber.*, 1899, 32, 2978—2987. Compare Abstr., 1898, i, 70 and 646).—A further discussion of the formulæ of these bromophenols. At present, it is impossible to decide whether a compound insoluble in alkalis of this type, for example,  $C_7H_7OBr$ , is represented by the



R. H. P.

**Bromophenols from *as-o*-Xylenol and *as-m*-Xylenol.** By KARL AUWERS (*Ber.*, 1899, 32, 2987—3005).—A comparison of the properties of the compounds described in the following three abstracts.

R. H. P.

**Pentabromide from [Pentabromo derivative of] *as-m*-Xylenol.** By KARL AUWERS and W. HAMPE (*Ber.*, 1899, 32, 3005—3016. Compare Abstr., 1896, i, 424, and 1897, i, 33).—The acetyl derivative of  $\omega\omega:2:5:6$ -pentabromo-1:3:4-xylenol,  $C_6Br_3(CH_2Br)_2 \cdot OAc$  (Zincke, Abstr., 1898, i, 70), forms colourless needles melting at  $180^\circ$ , and is easily reduced to the *acetyl* derivative of tribromo-1:3:4-xylenol, which crystallises from glacial acetic acid in lustrous prisms melting at  $115$ — $116^\circ$ .

$\omega\omega$ -*Diiodotribromo*-1:3:4-xylenol,  $C_6Br_3(CH_2I)_2 \cdot OH$ , prepared from the corresponding diacetate (m. p.  $172^\circ$ , *loc. cit.*) by treatment with hydrogen iodide, crystallises from glacial acetic acid in rosettes of small needles which melt at  $182$ — $183^\circ$ , and undergo gradual decomposition without previous solution when treated with aqueous alkalis. The same diacetate, on treatment with an excess of alkali, yields an insoluble, amorphous powder, the constitution of which could not be determined; on treatment with acetone, it yields a *substance* which melts at  $230$ — $232^\circ$ , and is probably the acetyl derivative of tribromo-4-hydroxy-*m*-xylylene glycol,  $OH \cdot C_6Br_3(CH_2 \cdot OH) \cdot CH_2 \cdot OAc$ .

The *glycol*, obtained by treating the dibromide with acetone and water, crystallises from benzene in slender needles melting at  $145$ — $146^\circ$ , and yields a *trimethyl ether* melting at  $95$ — $96^\circ$ , which, when treated with hydrogen bromide, yields *pentabromo*-1:3:4-xylenol *methyl ether*,  $C_6Br_3(CH_2Br)_2 \cdot OMe$ , melting at  $165$ — $168^\circ$ .

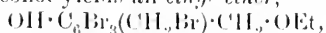
*Pentabromo*-1:3:4-xylenol, when treated with aniline in benzene solution, yields a  $\omega\omega$ -*dianilide*, which is a yellow, crystalline powder

melting at 118—121°. If the acetyl derivative of the pentabromo-compound is used, a *monoacetyl* derivative of the dianilide is obtained; it melts at 209°, is soluble in alkalis, and when boiled with acetic anhydride yields a *diacetate* insoluble in alkalis and melting at 116—118°. The *dipiperilide*, obtained in a similar manner, is a colourless, crystalline powder melting at 115—117°, and yields bromanil on oxidation with nitric acid. The diacetate (m. p. 172°), when oxidised in similar manner, yields a *tetrabromotoluquinone*,  $\text{CBr} \begin{smallmatrix} \text{CO} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{Br}$ , which crystallises in yellow, lustrous leaflets melting at 258—259°, and on reduction yields the corresponding *quinol*, which forms brownish needles melting at 226—227°.

R. H. P.

**Pentabromo-derivative of *as-o*-Xylenol.** By KARL AUWERS and R. VON ERGGELET [and in part H. VAN DE ROVAART and W. WOLFF] (*Ber.*, 1899, 32, 3016—3033).— $\omega\omega : 3 : 5 : 6$ -*Pentabromo-1 : 2 : 4-xylenol*,  $\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2 \cdot \text{OH}$ , obtained by heating tribromo-1 : 2 : 4-xylenol with an excess of bromine in a sealed tube at 130°, crystallises from glacial acetic acid in lustrous needles melting at 149—150°, and is insoluble in alkalis. The *acetyl* derivative melts at 127—128°, and is only slowly decomposed by boiling alkalis; on reduction, it yields the *acetyl* derivative of tribromo-1 : 2 : 4-xylenol (m. p. 111—112°).  $\omega : 3 : 5 : 6$ -*Tetrabromo-1 : 2 : 4-xylenol- $\omega$ -methyl ether*,  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OMe}$ , formed when the pentabromo-compound is boiled with methyl alcohol, melts at 132—133°, and is soluble in caustic soda solution. The *monoacetyl* derivative melts indefinitely between 86° and 90° and, if treated with sodium acetate and acetic anhydride, yields the *diacetate*,  $\text{OAc} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OAc}) \cdot \text{CH}_2 \cdot \text{OMe}$ , melting at 101—102°. The corresponding *ethyl ether* forms sharp-angled prisms melting at 124—125°, and yields a similar *diacetate* melting at 105—107°.

$\omega : 2 : 5 : 6$ -*Tetrabromo-1 : 2 : 4-xylenol*,  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OH}$ , prepared by treating the pentabromo-compound with acetone and water, crystallises from benzene in needles melting at 166—167°, and is soluble in alkalis. A poor yield of the corresponding *glycol* melting at 185° is obtained after further treatment with acetone. Its *dimethyl ether*,  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OMe})_2$ , is a colourless, crystalline powder melting at 157°. The *diethyl ether*, obtained by treating the monoethyl ether of the tetrabromo-xylenol with alcohol, crystallises in the form of compact prisms and cubes melting at 94°. The *triethyl ether* is a thick oil, which, on treatment with hydrogen bromide, yields *pentabromo-1 : 2 : 4-xylenol ethyl ether*,  $\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2 \cdot \text{OEt}$ , in the form of needles melting at 108—114°. The pentabromo compound, on treatment with sodium acetate and acetic acid, yields the *monoacetyl* derivative,  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OAc}$ , which crystallises in needles melting at 154—155°, forms a phenylurethane melting at 193°, and when boiled with alcohol yields an *ethyl ether*,



melting at 124—125°. The *diacetyl* derivative of the tetrabromo-compound forms small needles melting at 116°, and on treatment with

acetic anhydride yields the *triacetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OAc})_2$ , melting at  $133-134^\circ$ .

On treatment with *o*-toluidine, the pentabromo-compound is converted into the *di-o-toluidide* which melts at  $153^\circ$  and forms an *ethyl ether* melting at  $121-123^\circ$ .

The tetrabromo-compound, when treated with aniline in benzene solution, yields the compound  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OH}) \cdot \text{CH}_2 \cdot \text{NHPh}$ , which melts at  $171^\circ$  and forms a triacetyl derivative melting and decomposing at  $179-181^\circ$ .

*ω-Diiodotribromo-1:2:4-xyleneol*, prepared by treating the tetrabromo-compound previously described with hydrogen iodide, forms yellowish, compact crystals melting at  $165-166^\circ$ , and yields a *monoacetyl* derivative melting at  $142^\circ$ . On treatment with acetone, this diiodo-compound forms a *monoiodo*-derivative melting at  $193^\circ$ , the *diethyl ether* of which melts at  $110-111^\circ$ . The diiodo-compound, when treated with glacial acetic acid and sodium acetate, yields the *monoacetyl* derivative of the monoiodo-compound which melts at  $185-190^\circ$ . On reduction, the tetrabromo-xyleneol yields the *alcohol*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH}$  [ $= 1:2:4$ ]. This crystallises from benzene as silky needles melting at  $170-180^\circ$ , and yields a *diacetate* melting at  $135-137^\circ$ . The *monoacetyl* derivative,  $\text{OH} \cdot \text{C}_6\text{MeBr}_3 \cdot \text{CH}_2\text{OAc}$ , melts at  $140-142^\circ$ . On oxidation of the alcohol with nitric acid, tribromotoluquinone is obtained in the form of yellowish leaflets melting at  $233-235^\circ$ .  
R. H. P.

**Heptabromo-derivative of *as-o*-Xyleneol.** By KARL AUWERS and HARRY BURROWS [and in part H. VAN DE ROVAART] (*Ber.*, 1899, 32, 3034-3045).—*ωωωωω:3:4:6-Heptabromo-1:2:4-xyleneol*,  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CHBr}_2)_2$ , prepared by heating tribromo-1:2:4-xyleneol in a sealed tube at  $190^\circ$  with an excess of bromine, forms light, silver-grey crystals melting at  $199^\circ$ , and is insoluble in alkalis. The *acetyl* derivative melts at  $193^\circ$ , and is easily reduced to acetyltribromo-1:2:4-xyleneol. On boiling the heptabromo-derivative with methyl alcohol, the *dimethylacetal*,  $\text{CH}(\text{OMe})_2 \cdot \text{C}_6\text{Br}_3(\text{CHBr}_2) \cdot \text{OH}$  [ $= 1:2:4$ ], melting at  $116-118^\circ$ , is formed. The corresponding *diethyl acetal* melts at  $143^\circ$ . The corresponding *diacetate*, formed by treating the heptabromo-xyleneol with glacial acetic acid and sodium acetate, crystallises in colourless plates melting at  $155^\circ$ , and when boiled with acetic anhydride yields the *triacetyl* compound,  $\text{OAc} \cdot \text{C}_6\text{Br}_3(\text{CHBr}_2) \cdot \text{CH}(\text{OAc})_2$ , melting at  $132-133^\circ$ . When the acetals just described are warmed with glacial acetic acid, *ωω:3:4:6-pentabromo-5-hydroxy-o-tolualdehyde* is obtained; it crystallises in small needles melting at  $168^\circ$ , is soluble in alkalis, and forms an *acetyl* derivative melting at  $150^\circ$ . On oxidation with nitric acid, it yields *pentabromotoluquinone*,  $\text{CHBr}_2 \cdot \text{CBr}_3\text{O}_2$ , which crystallises from glacial acetic acid in yellow prisms melting at  $160^\circ$ . *3:4:6-Tribromo-5-hydroxy-o-tolualdehyde*, obtained by the reduction of the pentabromo-compound, forms small needles melting at  $187-188^\circ$ , and yields a *benzoyl* derivative melting at  $167-168^\circ$  and an *oxime* melting at  $207^\circ$ ; on oxidation, it yields *tribromotoluquinone* melting at  $234^\circ$ . Attempts were made to synthesise this aldehyde by brominating *p*-hydroxy-*o*-tolualdehyde. In this way,



4:6-dibromo-3-hydroxy-o-tolualdehyde is obtained; it forms small needles melting at 161—162°, yields an *oxime* melting at 197°, and is oxidised to 4:6-dibromo-3-hydroxy-o-toluic acid, which forms small, white needles melting at 232°. On further treatment with bromine, this aldehyde is converted into tetrabromo-*m*-cresol. This can also be prepared by the direct bromination of *m*-cresol or of *as*-oxylenol; it forms long, thin needles melting at 194°, is easily soluble in alkalis, and forms an *acetyl* derivative melting at 165—166°, and a *benzoyl* derivative melting at 153—154°; when treated with nitric acid, it yields tribromotoluquinone and an unstable *mononitro*-derivative melting at 88°.

Tribromo-*p*-hydroxyphthalaldehyde,  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{COH})_2$ , prepared by treating pentabromohydroxytolualdehyde with lime water, crystallises from dilute alcohol in the form of colourless needles and prisms melting at 202°, and yields an *acetyl* derivative melting at 205—209°. An isomeric substance melting at 245—247°, and forming an *acetyl* derivative melting at 218—220°, is obtained in small quantity in the preparation of this hydroxyphthalaldehyde. R. H. P.

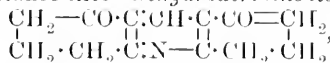
Catechol Derivatives. By CHARLES MOUREU (*Ann. Chim. Phys.*, 1899, [vii], 18, 76—139).—An account of work already published. (Compare Abstr., 1896, i, 215, 426, 477, 646; 1897, i, 336, 403; 1898, i, 411, 518, 644, 660; 1899, i, 30, 125, 433, 494, 679, 700.)

G. T. M.

Hydrogenised Derivatives of Diphenylmethane and Triphenylmethane. By DANIEL VORLÄNDER (*Annalen*, 1899, 309, 348—355).—An introductory paper (see following abstracts).

M. O. F.

Formaldehyde Derivative of Dihydroresorcinol. By DANIEL VORLÄNDER and FRITZ KALKOW (*Annalen*, 1899, 309, 356—374. Compare Merling, Abstr., 1894, i, 177, and Vorländer and Kalkow, Abstr., 1897, i, 513).—The *sodium* derivative of methylenebisdihydroresorcinol crystallises in prisms and contains  $2\text{H}_2\text{O}$ . The anhydride (*octohydroxanthenedione*) forms the *oxime*,  $\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}_3$ , which is microcrystalline, and melts at about 300°. Alcoholic ammonia converts methylenebisdihydroresorcinol into *decahydroacridinedione*, which has been described already. Nitrous acid transforms this substance into *octohydroacridinedione*,



which crystallises in white needles melting at 140—142°, and yields acridine when distilled with zinc dust; the *oxime* becomes brown above 200°, and melts and decomposes at 250°. A similar ketonic base,  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$ , obtained by distilling decahydroacridinedione, crystallises in flat needles and melts at 114°; the *hydrochloride* crystallises from water in colourless needles, and the *oxime* melts and decomposes at about 280°.

The ketonic acid,  $\text{C}_{13}\text{H}_{18}\text{O}_5$ , obtained from methylenebisdihydroresorcinol and caustic alkali, forms anhydrous *barium*, *silver*, and

lead salts; the *orime* and *semicarbazone* melt at  $159^{\circ}$  and  $218^{\circ}$  respectively, and the *diethyl* ester boils at  $235\text{--}240^{\circ}$  under 24 mm. pressure.

*Methylenebismethylldihydroresorcinol*,  $C_{15}H_{20}O_4$ , and *methylenebisdimethylldihydroresorcinol*,  $C_{17}H_{24}O_4$ , melt at  $152^{\circ}$  and  $187\text{--}188^{\circ}$  respectively; the latter yields *tetramethyloctohydroxanthenedione*,  $C_{17}H_{22}O_3$ , which melts at  $171^{\circ}$  and, with alcoholic ammonia, forms *tetramethyldecahydroacridinedione*.

*Methylenebisphenyldihydroresorcinol*,  $C_{25}H_{24}O_4$ , melts at  $212^{\circ}$ ; *diphenyloctohydroxanthenedione*,  $C_{25}H_{22}O_3$ , melts at  $225\text{--}226^{\circ}$ .

*Pentamethyloctohydroxanthenedione*,  $C_{15}H_{24}O_3$ , from dimethyldihydroresorcinol and acetaldehyde, melts at  $174^{\circ}$ . *Ethyltetramethyloctohydroxanthenedione*,  $C_{16}H_{20}O_3$ , melts at  $139^{\circ}$ . *Hexamethyloctohydroxanthenedione*,  $C_{19}H_{26}O_3$ , melts at  $245^{\circ}$ .  
M. O. F.

### Compounds of Dihydroresorcinol with Aromatic Aldehydes.

By DANIEL VORLÄNDER and O. STRAUSS (*Annalen*, 1899, 309, 375—383).—*Benzylidenebisdihydroresorcinol*,  $C_{19}H_{20}O_4$ , prepared from dihydroresorcinol and benzaldehyde, melts and decomposes at  $208^{\circ}$ , *phenyloctohydroxanthenedione*,  $C_{19}H_{18}O_3$ , melts at  $255^{\circ}$ , and the *p*-nitro-derivative, obtained from *p*-nitrobenzaldehyde, dihydroresorcinol, and glacial acetic acid, melts at  $246^{\circ}$ . *Phenyldecahydroacridinedione*,  $C_{19}H_{19}O_2N$ , produced on heating phenylhydroxanthenedione with alcoholic ammonia, does not melt below  $310^{\circ}$ , and forms, in alcohol, a colourless solution which exhibits blue fluorescence; distillation with zinc dust gives acridine.

*Benzylidenebisdimethylldihydroresorcinol*,  $C_{23}H_{28}O_4$ , obtained from dimethyldihydroresorcinol and benzaldehyde, melts at  $193^{\circ}$ ; *phenyltetramethyloctohydroxanthenedione*,  $C_{23}H_{26}O_3$ , melts at  $200^{\circ}$ . *Criminyldienebisdimethylldihydroresorcinol*,  $C_{26}H_{32}O_3$ , melts at  $173^{\circ}$ .

*Benzylidenebisphenyldihydroresorcinol*,  $C_{31}H_{28}O_4$ , melts at  $125^{\circ}$ , water being eliminated; *triphenyloctohydroxanthenedione*,  $C_{31}H_{26}O_3$ , is identical with "benzylidenephenyldihydroresorcinol" (Vorländer and Erig, *Abstr.*, 1897, i, 275), and melts at  $230^{\circ}$ . *Triphenyldecahydroacridinedione*,  $C_{31}H_{27}O_2N$ , forms red solutions having green fluorescence.

M. O. F.

**Tautomerism of Isatin.** By LEO MARCHLEWSKI (*J. pr. Chem.*, 1899, [ii], 60, 407—408. Compare *Abstr.*, 1896, i, 96 and 235).—When isatin reacts with *o*-phenylenediamine acetate in acid solution, a mixture of indophenazine and *o*-aminophenimesatine is formed; as the imesatine cannot be converted into the indophenazine under the conditions employed, it is clear that the isatin acts as a mixture of lactam and lactim.

Acids, such as acetic acid, appear to be able to cause the conversion of the lactim into lactam, as isatin when condensed with *o*-phenylenediamine in 50 per cent. acetic acid solution gives only a trace of imesatine, whilst the latter changes only excessively slowly into indophenazine when boiled with acetic acid of that strength.  
A. L.

**Optically Active *trans*-Hexahydrophthalic Acids.** By ALFRED WELNER and H. E. CONRAD (*Ber.*, 1899, 32, 3046—3055).—*trans*-Hexahydrophthalic acid is a racemic compound and is resolved

into its optically active components by fractional crystallisation of its quinine salts in alcoholic solutions; the neutral salt of the dextro-rotatory acid separates first, whilst the acid salt of the levorotatory acid remains dissolved. The anhydrides of the optically active acids, prepared by heating these compounds with acetic chloride, crystallise in broad plates, whilst the corresponding racemic compound separates in needles. The dimethyl esters were produced by heating the acids with methyl alcohol containing hydrogen chloride; the monomethyl esters were obtained by warming the anhydrides with methyl alcohol. The *monoamide* of the racemic acid was prepared by passing dry ammonia into an acetone solution of the inactive anhydride; it melts at 196°.

Active <i>trans</i> hexahydrophthalic acids and derivatives.	$[\alpha]_D$ .	M.p.	M.p. of racemic compound.
<i>d-trans</i> -Acid .....	18.2°	178—183°	215°
<i>l</i> - „ .....	-18.5°		
<i>d</i> -Anhydride .....	-76.7°	164°	140
<i>l</i> - „ .....	75.8°		
<i>d</i> -Dimethyl ester ...	28.7°	below 0°	33
<i>l</i> - „ .....	-29.6°		
<i>d</i> -Monomethyl ester.	26.5°	39°	96
<i>l</i> - „ .....	-24.8°		

*cis*-Hexahydrophthalic acid is not resolved into active components by the aid of quinine, cinchonine, or coniine; this acid differs from its *trans*-isomeride in forming the *acid potassium* salt,  $C_8H_{11}O_4K + 3H_2O$ .  
G. T. M.

**Constitution of Santonic and Metasantonic Acids and of Metasantonin.** By LUIGI FRANCESCONI (*Gazzetta*, 1899, 29, ii, 181—257. Compare Abstr., 1898, i, 267).—A detailed account is given of the various transformations of santonic and metasantonic acids and of metasantonin.

*Santonic acid dioxime*,  $C_{15}H_{22}O_4N_2$ , is a white, friable substance which melts and decomposes at 120—125°; it dissolves readily in dilute halogen hydracids, alcohol, or ether. Its specific rotatory power is  $[\alpha]_D -102.4^\circ$ . It gives a *barium* salt,  $(C_{15}H_{21}O_4N_2)_2Ba$ .

With excess of phenylhydrazine, santonic acid gives the *phenylhydrazone* of *santonic acid phenylhydrazide*,  $C_{27}H_{32}O_2N_4$ , which is an orange-yellow powder melting and decomposing at 95°; it is readily soluble in alcohol, ether, or acetic acid.

*Triketosantonic acid*,  $\begin{array}{c} CO \cdot CMe \cdot CH \cdot CO \cdot C \cdot OH \\ CO \cdot CMe \cdot CH \cdot CO \cdot C \cdot CHMe \cdot CO_2H \end{array}$  obtained by the action of bromine on santonic acid, forms glistening, straw-yellow needles melting and decomposing at 234°; it is readily soluble in ethyl acetate, alcohol, or water, the aqueous solution having an intense yellow colour. Its specific rotatory power in alcohol is  $[\alpha]_D -458.7^\circ$ . The *barium* salt,  $C_{15}H_{12}O_7Ba + 2H_2O$ , is a golden-yellow substance. The *ethyl* ester,  $C_{14}H_{13}O_5 \cdot CO_2Et$ , forms glistening, pale yellow needles which melt at 157—158° and dissolve readily in

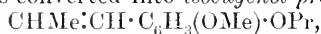
ethyl acetate or alcohol; the specific rotation in alcohol is  $[\alpha]_D -39.4^\circ$ . The *dioxime*,  $C_{15}H_{14}O_5(NO)_2$ , is a hard, friable substance of a straw-yellow colour and is readily soluble in ether, alcohol, or water. The *anhydride* of the dioxime,  $C_{15}H_4O_5 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} > O$ , is a hard, friable, orange-coloured mass which softens at about  $130^\circ$ , melts and decomposes at  $140^\circ$ , and dissolves in the ordinary solvents.

*Tribromo- $\alpha$ -santonin*,  $C_{15}H_{15}O_3Br_3$ , obtained by the action of bromine on santonin acid, melts at  $187-188^\circ$  and dissolves in ethyl acetate and to a less extent in ether, but is insoluble in solutions of alkali carbonates.

T. H. P.

**Action of Sodium Methoxide on Dibromides of Propenyl Compounds and of Unsaturated Ketones.** By F. J. POND, O. P. MAXWELL, and G. M. NORMAN (*J. Amer. Chem. Soc.*, 1899, 21, 955—967. Compare Pond and Beers, *Abstr.*, 1898, i, 645).—When isopropyl dibromide (Ciamician and Silber, *Abstr.*, 1890, 1294) is treated with sodium methoxide according to the method previously described, a ketone,  $COEt \cdot C_6H_3(OMe)_2 \cdot O_2 \cdot CH_2$ , is obtained which crystallises from alcohol in colourless prisms melting at  $95.5^\circ$ ; its *oxime* crystallises from methyl alcohol in colourless needles melting at  $124^\circ$ , and is readily reconverted into the ketone when heated with dilute sulphuric acid on the water-bath. The constitution of the ketone follows from the fact that it yields propionic acid when heated at  $250^\circ$  with concentrated sulphuric acid.

Eugenol propyl ether,  $OPr \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH:CH_2$ , is a colourless oil boiling at  $270.5^\circ$  and having a sp. gr. 1.0032. Cahours (this *Journ.*, 1877, i, 461) gives its boiling point as  $263-265^\circ$ ; when boiled with alcoholic potash, it is converted into *isoeugenol propyl ether*,



which distils at  $280-281^\circ$  and forms large, colourless prisms melting at  $53-54^\circ$ ; it may also be obtained by the action of propyl bromide on the potassium salt of isoeugenol. Its *dibromide* melts at  $53-54^\circ$ , is readily soluble in alcohol or ether, but cannot be recrystallised without decomposing; when treated with sodium methoxide, it yields the *ketone*,  $COEt \cdot C_6H_3(OMe) \cdot OPr$ , which, after distillation under reduced pressure, crystallises from methyl alcohol in large prisms melting at  $63-64^\circ$ , and boiling with slight decomposition at  $284-287^\circ$  under atmospheric pressure. The *oxime*,  $C_{13}H_{13}O_3N$ , forms large crystals melting at  $114^\circ$ .

Benzylideneacetophenone (Claisen and Claparède, *Abstr.*, 1882, 512) yields a *dibromide* crystallising in small prisms and melting at  $156^\circ$ ; this dibromide is converted by the action of sodium methoxide into dibenzoylmethane (Baeyer and Perkin, *Abstr.*, 1884, 64; Claisen, *ibid.*, 1887, 575).

An unstable oil, probably the unsaturated ether  $OMe \cdot CPh:CHBz$ , has been isolated as an intermediate product; on treatment with dilute acids, it yields dibenzoylmethane.

*Anisylideneacetophenone* crystallises in fine, yellow needles melting at  $77-78^\circ$ ; its *dibromide* crystallises in white prisms melting at  $140-141^\circ$ , and on treatment with sodium methoxide yields *anisoyl-*

*benzoylmethane*,  $C_{16}H_{14}O_3$ , crystallising in plates and melting at  $131-132^\circ$ . Bromine converts the diketone into a *bromine* derivative melting at  $127-128^\circ$ . J. J. S.

**$\alpha$ -Oximinoketones and Quinoneoximes as Pseudo-acids.** By R. C. FARMER and ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3101—3109).—The criteria enumerated in this vol., i, 95, are applied to the cases in question. Isonitrosoacetone,  $NOH:CH:CMcO$ , is neutral to litmus, is not appreciably dissociated, and does not form a compound with dry ammonia. But the sodium salt exhibits on dilution an increase of conductivity,  $\Delta_{1024-32}$ , only a little greater than in the case of salts of strong acids, and it is only slightly hydrolysed in aqueous solution. Consequently, isonitrosoacetone is a pseudo-acid, and its sodium salt has a different constitution, either  $NO:CH:CMcONa$ ,  $CMc \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} N:ONa$ , or  $ONa:CMc \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} N$ .

Quinonemonoxime,  $NOH:C_6H_4:O$ , does not unite with ammonia in benzene, and very slowly in ethereal solutions; but its sodium salt exhibits the normal increase of conductivity on dilution,  $\Delta_{1024-32}$ ; it must therefore be the salt of a comparatively strong acid, and hence quinoneoxime is a pseudo-acid. Quinonoxime, in aqueous solution, has a decided acid reaction and a moderately large dissociation constant, and its very dilute solution has the same (greenish-yellow) colour as equivalent solutions of the red sodium (with  $2\frac{1}{2}H_2O$ ) and green potassium salts (with  $1H_2O$ ); hence the oxime itself undergoes a partial transformation in aqueous solution and the case is one of 'ionisation isomerism.' Quinonedioxime, on the other hand, has no appreciable conductivity, and its sodium salt is a true oxime salt, for it is largely hydrolysed in aqueous solution, as the abnormally large increase in conductivity on dilution,  $\Delta_{1024-32}$ , shows; indeed, the solution gradually deposits an *anhydride*,  $(C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix})_n$ , a bright-red, amorphous, very stable substance. *o*-Toluquinoneoxime resembles its lower homologue, and "nitroso-oreinol" forms a very strongly acid solution. C. F. B.

**Space Isomerism of the Ethers of Toluquinoneoxime.** By W. CONGER MORGAN (*Amer. Chem. J.*, 1899, 22, 402—407).—The benzoyl derivative of toluquinone-*m*-oxime melting at  $139^\circ$  (Bridge and Morgan, *Abstr.*, 1899, i, 130) is completely converted into the stereoisomeride melting at  $193^\circ$  by heating with alcohol in a sealed tube for 3 hours at  $120^\circ$ ; the latter, under similar conditions, is not changed, but on raising the temperature to  $150^\circ$ , is completely decomposed. Caustic alkalis hydrolyse the compound of lower melting point to the corresponding oxime, which, however, on treatment with benzoyl chloride, yields the modification of higher melting point exclusively; the latter appears from these experiments to be the more stable form.

The phenomena described by Bridge and Morgan have been reproduced completely in the ethers formed by the interaction of acid chlorides with the sodium salt of the oxime prepared by the action of amyl nitrite on the sodium salt of *o*-cresol; since there is no

possibility of a nitro-compound being formed under these conditions, although this is not precluded in the action of nitrous acid on the cresols, the lower melting stereoisomerides cannot be considered as merely the higher melting compounds rendered impure by such admixture.

The *benzoate*,  $C_{14}H_{10}O_3NBr$ , of bromotoluquinone-*o*-oxime, prepared by boiling the corresponding dibromide,  $C_{14}H_{11}O_3NBr_2$  (Bridge and Morgan, *loc. cit.*), with 75 per cent. alcohol, forms yellow crystals and melts at  $184^\circ$ . The *dichloride*,  $C_{14}H_{11}O_3NCl_2$ , of toluquinone-*o*-oxime benzoate crystallises from glacial acetic acid in short, thick, colourless prisms and melts at  $149^\circ$ ; when boiled with dilute alcohol, it loses hydrogen chloride and yields *chlorotoluquinone-*o*-oxime benzoate*,  $C_{14}H_{10}O_3NCl$ , which forms yellow crystals and melts and decomposes at  $185$ – $193^\circ$ . All these compounds appear to exist in one form only.

W. A. D.

**Isomerism in the Menthol Series.** By IWAN L. KONDAKOFF and EUGEN LUTSCHININ (*J. pr. Chem.*, 1899, [ii], 60, 257–279).—Menthyl iodide, prepared by the action of hydriodic acid on either menthol or menthomenthene, boils at  $124$ – $126^\circ$  under a pressure of 18 mm., and has a sp. gr. 1.3836 at  $0^\circ$  and 1.3155 at  $16.5^\circ$ . It acts very rapidly on moist silver oxide, yielding tertiary menthomenthol; the passage from secondary menthol to tertiary menthomenthol is closely analogous to that from methylisopropylcarbinol to dimethylethylcarbinol.

Dihydrocarvone, prepared by oxidising the dihydrocarveol from *l*-carvone, boils at  $221$ – $224^\circ$ , has a sp. gr. 0.9308 at  $16^\circ$ , a refractive index  $n_D$  1.47243, the molecular refraction being 45.78; its specific rotation is  $[\alpha]_D +17^\circ 27.5'$ . The constants obtained for the product from *d*-carvone were as follows: boiling point,  $221$ – $222^\circ$ ; sp. gr. 0.9269 at  $22^\circ$ , refractive index  $n_D$  1.46998, molecular refraction 45.80, and specific rotatory power  $[\alpha]_D -19^\circ 3.5'$ . This dihydrocarvone is readily reduced by sodium and alcohol to pure dihydrocarvol boiling at  $224$ – $225^\circ$ , and is readily converted into carvenone by Kondakoff and Gorbunoff's method (*Abstr.*, 1898, i, 145); the latter substance boils for the most part at  $231$ – $233^\circ$  under 763 mm., and at  $101$ – $103^\circ$  under 10 mm. pressure, but invariably leaves a residue which boils at  $233$ – $240^\circ$ .

Klages' observation that carvenone may be obtained by treating dihydrocarvone with formic acid (*Abstr.*, 1899, i, 624) is the natural outcome of the work of Kondakoff and Gorbunoff; it is not necessary, however, to use anhydrous formic acid or to prolong the action; the product obtained by this method boils at  $232^\circ$  under 759 mm. pressure, and not at  $232$ – $235^\circ$  as stated by Klages.

Carvomenthol, obtained by reducing carvenone by Wallach's process (*Abstr.*, 1894, i, 44), boils at  $220$ – $221^\circ$  under 762 mm. pressure, but contains a fraction boiling at  $240^\circ$ ; it has a sp. gr. 0.9070 at  $20.2^\circ$ ; its refractive index is  $n_D$  1.4672, its molecular refraction being 47.49. The foregoing carvomenthol was purified by conversion into tetrahydrocarvone as recommended by Wallach, but much loss is experienced in this process. The substance now boiled at  $222^\circ$ , had a

sp. gr. 0.9010 at 23°, a refractive index  $n_D$  1.4696, and a molecular refraction 47.58.

Carvomenthol, prepared from specimens of active carone, varies considerably in optical activity, as do the derivatives prepared from it.

*Carvomenthyl acetate*,  $C_{10}H_{19}OAc$ , boils at 235—238° under 761 mm. pressure, and at 105—107° under 11 mm.; it is a colourless, fairly mobile liquid having a faint odour of cherries; it has a sp. gr. 0.9280 at 22°/4°, a refractive index  $n_D$  1.45079, a molecular refraction 57.42 its specific rotation being  $[\alpha]_D + 4.7'$ .

*Carvomenthyl chloride*,  $C_{10}H_{19}Cl$ , is colourless and has an odour resembling menthyl chloride; it boils at 90—95° under 15 mm. pressure, and at 82—85° under 11 mm., is optically inactive, has a sp. gr. 0.9450 at 21°/4°, and refractive index  $n_D$  1.46534 at 21°, the molecular refraction being 50.48. The *bromide*,  $C_{10}H_{19}Br$ , is colourless, boils at 95—99° under 10 mm. pressure, has a sp. gr. 1.1870 at 21°, a refractive index  $n_D$  1.49060 at 21°/21°, and a molecular refraction 53.39.

Carvomenthene, prepared by heating carvomenthyl chloride or bromide with alcoholic potash, is divisible in two portions by fractional distillation, about 90 per cent. of the whole distilling at 172—174.5°, and the rest at 174.5—178°. It is a colourless, mobile liquid having an odour of menthene, is altered by exposure to air, and reacts readily with permanganate and with bromine.

The portion of the carvomenthene of lower boiling point has a sp. gr. 0.8230 at 16.5°/4°, a refractive index  $n_D$  1.45979, molecular refraction 45.68, and a specific rotation  $[\alpha]_D - 2.4'$ . The fraction of higher boiling point had a sp. gr. of 1.8230 at 19°/4°, a refractive index  $n_D$  1.46108, a molecular refraction 45.89, and a specific rotatory power  $[\alpha]_D - 1.28$ .

*Carvomenthene hydrochloride* boils at 90—98° under 18 mm., and at 89—95° under 16 mm. pressure; it has a sp. gr. 0.9390 at 19°/4°, a refractive index  $n_D$  1.464941, the molecular refraction being 50.95, whilst its specific rotatory power is  $[\alpha]_D - 1.22'$ . Its properties are thus identical with those of carvomenthyl chloride, with the exception of the rotatory power.

Baeyer has shown (Abstr., 1893, i, 722) that carvomenthene combines with hydrogen bromide or iodide in the cold, yielding tertiary halogen derivatives, convertible through the intermediary of the corresponding acetates into a mixture of carvomenthene and tertiary carvomenthol. The authors have prepared the bromo-compound by heating the hydrocarbon with strong hydrobromic acid at 160—170°; it boils at 92—98° under 10 mm. pressure, has a sp. gr. 1.1620 at 20.5°/4°, a refractive index  $n_D$  1.48822 at 20.5°, and a molecular refraction 51.27; it is optically inactive. Its properties are almost identical with those of carvomenthyl bromide, but it is highly probable that it consists of a mixture of the secondary and tertiary bromo-compounds, derived from two isomeric carvomenthenes in the parent hydrocarbon. The carvomenthene regenerated from the hydrobromide boiled at 172—175°, had a sp. gr. 0.8230 at 20°/4°, a refractive index  $n_D$  1.45959, a molecular refraction 45.69, and a specific rotatory power  $[\alpha]_D - 0.23'$ .

Carvomenthyl chloride or bromide, on treatment with moist silver

oxide, affords tertiary carvomenthol and a small quantity of a substance,  $C_{10}H_{22}O_3$ , which crystallises in slender needles and melts at  $101-102^\circ$ .

It is not improbable that the behaviour of menthomenthol and carvomenthol illustrates a general law whereby hydro-aromatic alcohols containing the group  $\cdot CHR \cdot CH(OH) \cdot$  are converted by halogen hydrides into tertiary halogen derivatives. The behaviour of fenchyl alcohol in this respect is being investigated. A. L.

**Solubility of Camphor in Hydrochloric Acid.** By AL. J. ZAHARIA (*Chem. Centr.*, 1899, ii, 308; from *Bul. soc. Sci. Bucuresci*, 1899, 8, 53-61).—Camphor is rather soluble in water and the aqueous solution becomes turbid on addition of sodium carbonate or sodium chloride solution. Camphor is very soluble in concentrated hydrochloric acid, and the more concentrated the acid and the lower the temperature the greater the quantity dissolved. On account of the volatility of camphor, the amount dissolved could not be determined. A saturated solution containing 35.74 per cent. of hydrochloric acid has a sp. gr. 1.1405. The acid solution of pure camphor is orange-yellow, and of impure camphor reddish-yellow, changing gradually to deep-red. Any excess of camphor is coloured light brown and may be dissolved with the exception of a small resinous residue by adding more hydrochloric acid. When a few drops of nitric acid are added to the hydrochloric acid solution, an oil separates which, when distilled or treated with water, again forms camphor. By electrolysis the hydrochloric acid solution, hydrogen is liberated at the cathode and a liquid is quickly formed at the anode, which by exposure to the air or treatment with water regenerates camphor. The amount of camphor in solution could not be determined polarimetrically, for the rotatory power depends on the quantity of hydrochloric acid present. When chlorine is passed into a hydrochloric acid solution of camphor, an oil is very slowly formed.

Camphor appears to behave towards hydriodic acid in a similar way. E. W. W.

**Nitroso-derivatives of Caryophyllene and Cadinene and their bearing on the Characterisation and Classification of the Sesquiterpenes.** By OSWALD SCHREINER and EDWARD KREMERS (*Pharm. Archives*, 1899, 2, 273-300. Compare *Abstr.*, 1899, i, 619).—A pure specimen of caryophyllene, boiled at  $136-137^\circ$  under 20 mm. pressure, had a sp. gr. 0.90301 at  $20^\circ/20^\circ$ , index of refraction  $n_D$  1.49976 at  $20^\circ$ , and specific rotatory power  $[\alpha]_D - 8.959$  at  $20^\circ$ . The nitrosite is not polymerised, but has the simple formula  $C_{15}H_{24}O_3N_2$ , as shown by cryoscopic determinations in benzene solution; it has a specific rotatory power  $[\alpha]_D$  of about +103 in 1.6 per cent. benzene solution, and, with benzylamine, it yields a product which melts at  $167^\circ$ . When exposed to sunlight in absolute alcoholic solution, it is transformed into a colourless ( $\alpha$ ) isomeride with the same molecular weight; this melts at  $113-114^\circ$ , is soluble in alcohol and benzene, and has no appreciable optical activity. When the nitrosite is exposed to sunlight in benzene solution, another colourless ( $\beta$ ) substance is formed, which melts at  $146-148^\circ$ , and is insoluble in benzene or



alcohol; the yellow-orange rays are most active in effecting this change. The nitrosochloride can be obtained crystalline by mixing caryophyllene, alcohol, ethyl acetate, and ethyl nitrite, cooling in a freezing mixture, adding saturated alcoholic hydrogen chloride, leaving the whole in the cold for an hour, and then exposing it to sunlight; it melts and decomposes at  $158^{\circ}$ , and has the bimolecular formula  $(C_{15}H_{24}ONCl)_2$ ; with benzylamine, it forms two derivatives,  $\alpha$  and  $\beta$ , melting at  $167^{\circ}$  and  $128^{\circ}$  respectively; the former is the less soluble in alcohol. The nitrosate is also bimolecular; with benzylamine, it yields a product, melting at  $128^{\circ}$ , identical with the  $\beta$ -product obtained from the nitrosochloride. The hydrochloride of caryophyllene can be obtained crystalline by saturating an ethereal solution of the sesquiterpene with hydrogen chloride, and exposing the solution to intense cold; it melts at  $69-70^{\circ}$ .

When cadinene is mixed with glacial acetic acid, cooled with a freezing mixture, ethyl nitrate added, the mixture treated with strong nitric and glacial acetic acids, and diluted with alcohol, cadinene *nitrosate*, melting and decomposing at  $105-110^{\circ}$ , is precipitated. When a saturated solution of hydrogen chloride in glacial acetic acid is added, instead of the nitric and acetic acids, a *nitrosochloride*, melting and decomposing at  $93-94^{\circ}$ , is obtained.

C. F. B.

**Oil and Terpenes from *Aralia nudicaulis*.** By WILLIAM C. ALPERS (*Chem. Centr.*, 1899, ii, 623; from *Amer. J. Pharm.*, 71, 370-378).—The fresh root of *Aralia nudicaulis* contains 40-60 per cent. of water, and the dry drug yields on an average 5.53 per cent. of ash, which contains about 1.38 per cent. of sodium and potassium chlorides and sulphates. The dark red, fatty oil, obtained by extraction, has a sp. gr. 0.921 at  $20^{\circ}$ , is soluble in light petroleum, benzene, ether, or chloroform, slightly so in absolute alcohol, and insoluble in water; it solidifies at  $3^{\circ}$ , has acid number 7.3, saponification number 192, iodine number 106, and molecular weight of about 900; it consists chiefly of triolein. About 0.12 per cent. of an oil is obtained by distilling finely powdered aralia with steam; it has a pleasant, aromatic odour, and is composed mainly of a sesquiterpene, *araliene*,  $C_{15}H_{14}$ , which boils at  $270^{\circ}$ , has a sp. gr. 0.9086 at  $20^{\circ}$ , a specific rotatory power  $[\alpha]_D -7$  to  $-8$ , and a refractive index  $n_D 1.49936$ . It combines with hydrogen chloride to form an oily hydrochloride, but does not yield a solid bromide by the action of bromine. With a solution of hydrogen chloride in glacial acetic acid, it forms a bluish compound. The ethereal oil also contains a small quantity of a sesquiterpene alcohol, and a little azulene,  $C_{15}H_{26}O$ , which boils at about  $300^{\circ}$ .

E. W. W.

**Liquorice Oil.** By HEINRICH HAENSEL (*Chem. Centr.*, 1899, ii, 624; from *Pharm. Centr.-H.*, 40, 533).—By distilling Spanish liquorice root (*Glycyrrhiza glabra*), 0.03 per cent. of an ethereal oil is obtained; the Russian roots yield 0.035 per cent. These oils have a feeble acid reaction, which is possibly due to glycyrrhizic acid, but their composition is not identical, for whilst the Russian oil is dextrorotatory, the Spanish is laevorotatory.

E. W. W.

**Ethereal Oil of Poplar Buds.** By FRITZ FICHTER and E. KATZ (*Ber.*, 1899, 32, 3183—3185).—The principal fraction obtained by distilling oil of poplar buds under diminished pressure is a terpene boiling at 132—137° under 13 mm. pressure, and at 263—269° under ordinary pressure; it has a sp. gr. 0.8926 at 15°/4°, and a specific rotatory power 10°48' at 22°; its vapour density corresponds with that of a sesquiterpene,  $C_{15}H_{24}$ .

The *nitrosochloride*,  $C_{15}H_{24} \cdot NOCl$ , obtained from the sesquiterpene and amyl or ethyl nitrite, and hydrochloric acid, separates as a crystalline powder from its solution in benzene or chloroform on the addition of methyl alcohol; it melts indefinitely, the range of temperature being 164—170°.

The *nitrolpiperidine* from the preceding compound and piperidine crystallises from alcohol and melts at 151—152°; the *nitrolbenzylamine* crystallises from alcohol in needles and melts at 132—133°; the *chlorides* of these substances have the composition  $C_{15}H_{24}ON \cdot C_5NH_{10} + HCl$  and  $C_{15}H_{24}ON \cdot NH \cdot CH_2Ph + HCl$  respectively.

The *nitroso-* or *isonitroso-sesquiterpene*,  $C_{15}H_{22} \cdot NOH$ , is obtained as an oil on treating the nitrosochloride with sodium ethoxide; on reduction, this substance yields an aminosesquiterpene.

The *nitrosite*, produced by the action of nitrous acid on the sesquiterpene, separates at first in blue needles melting at 127°; after crystallisation from alcohol, it becomes colourless and melts at 172°.

The *nitrosate* from the sesquiterpene, amyl nitrite, and nitric acid, crystallises from benzene and melts at 162—163°. The sesquiterpene does not yield crystalline additive compounds with bromine, hydrogen bromide, or hydrogen chloride, neither does it combine with elements of water (Wallach, *Abstr.*, 1893, 101). The properties of the sesquiterpene of poplar buds and its derivatives resemble those of the humulene in oil of hops (Chapman, *Trans.*, 1895, 67, 57 and 780). On the other hand, the sesquiterpene, although it may contain humulene, cannot consist wholly of this hydrocarbon, for the former is optically active whilst the latter is inactive.

The higher fractions of poplar oil contain a mixture of paraffins, "stearoptenes," consisting of the hydrocarbon  $C_{24}H_{50}$  and its higher homologues; the total amount of paraffin in the oil is only  $\frac{1}{2}$  per cent.

G. T. M.

**Glucosides and Enzymes contained in the Root of some Spiræas.** By MARTINUS W. BEYERINCK (*Chem. Centr.*, 1899, ii, 259; from *Centr. Bakt. Parasitenk.*, [ii], 5, 425—429).—The roots, rhizomes, and lower portions of *Spiræa ulmaria*, *S. filipendula*, and *S. palmata* contain a glucoside, gaultherin, and an enzyme, gaultherase, and by the interaction of these compounds methyl salicylate is formed. The elder portions of the roots and rhizomes of *S. kamschatica* also contain a second glucoside, spiræin, which is decomposed by gaultherase, forming salicylaldehyde. Gaultherin is prepared from the root nodules of *S. filipendula* by treating with boiling alcohol or boiling water, which dissolves the glucoside, but decomposes the enzyme. The glucoside could not be obtained in a crystalline form. Gaultherase, prepared from the same root by allowing the enzyme to

act on the glucoside and then extracting with alcohol, is soluble in water. It is not identical with emulsin, since it does not act on salicin or amygdalin, and gaultherin is not attacked by emulsin. By distilling the decomposition products formed in the production of gaultherase in steam, gaultheria oil is obtained. Hydrocyanic acid could not be detected in the products of the decomposition of gaultherin or of spiræin.

The presence of even 0.1 per cent. of gaultheria oil prevents the growth of mould. The odoriferous substances contained in plants may serve to protect them from insects. The merest traces of Capuchin oil are sufficient to prevent the growth of *Saccharomyces mycoderma*, but this oil has very much less effect on the lactic acid ferment or on acetic acid bacteria. This preventive action may be due to the presence of a hydroxybenzylthiocarbimide. E. W. W.

**Derride and Pachyrhizide : Indian Fish Poisons.** By H. E. TH. VAN SILLEVOLDT (*Chem. Centr.*, 1899, ii, 588—589; from *Ned. Tijds. Pharm.*, 11, 246—256; and *Arch. Pharm.*, 1899, 237, 595).—The stupefying fish poisons occur mainly in plants of the family of *Papilionaceæ*. Derride,  $C_{33}H_{30}O_{10}$ , prepared from the root of *Derris elliptica*, Benth., by treating with water, extracting with alcohol, evaporating, and treating the residue with ether, is a pale yellow substance, melts at  $73^{\circ}$ , and is easily soluble in the usual organic solvents, slightly so in light petroleum, and insoluble in water. The alcoholic solution has a faintly acid reaction. Derride is dissolved by sulphuric acid, forming a brownish-violet solution, from which it is reprecipitated by water, and it appears to combine with phenylhydrazine. By boiling with an alcoholic solution of hydrogen chloride, it forms an anhydro-derivative,  $C_{33}H_{28}O_9$ , which is also present in crude derride, and is not dissolved by ether. This compound forms small needles, melts at  $214^{\circ}$ , and when treated with hydriodic acid forms a compound,  $C_{30}H_{19}O_6(OH)_3$ , which melts at  $240^{\circ}$ .

The preparation of pachyrhizide,  $C_{30}H_{24}O_{10}$ , from the seeds of *Pachyrhizus angulatus*, Rich., is similar to that of derride. Pachyrhizide melts at  $81^{\circ}$ , and closely resembles derride. A compound,  $C_{29}H_{20}O_9$ , which is insoluble in ether and melts at  $196^{\circ}$  is also contained in the seeds. The anhydro-derivative of pachyrhizide,  $C_{30}H_{22}O_9$ , obtained by warming it with an alcoholic solution of hydrogen chloride, is a crystalline substance, melts at  $182^{\circ}$ , combines with phenylhydrazine, and contains two methoxy-groups.

Derride and pachyrhizide appear to belong to the same homologous series as Pfaff's timboin (Abstr., 1891, 938), for which the formula  $C_{34}H_{32}O_{10}$  may be calculated from his analyses. E. W. W.

**Chlorophyll.** By G. BODE (*J. pr. Chem.*, 1899, [ii], 60, 385—396).—A reply to Marchlewski (Abstr., 1899, i, 381).

**Phylloxanthin.** By G. BODE (*Chem. Centr.*, 1899, ii, 529; from *Bot. Centr.*, 20, 227—239).—A continuation of the controversy with Marchlewski (Abstr., 1899, i, 381). The alcoholic plant extract which contains chlorophyll combined with a lecithin is named crude

chlorophyll solution. By the action of weak acids, this compound undergoes an intramolecular change, being converted into the crystalline, orange-green chlorophyllan, and by the action of alkalis or of strong acids is decomposed into the leucotin constituents and alkali or acid compounds of chlorophyll. The latter Marčulewski's alkali-chlorophyll and phyllopyranon are decomposed by water. The chlorophyll compounds have different colours according to the nature of the solvent and the concentration, which determine whether the compound remains undecomposed or is resolved into its components (Oswald and J. Wagner-Jauregg). Marčulewski's phyllopyranon is impure chlorophyllan and, like phyllopyranon, is a really a chlorophyll derivative, whilst phyllopyrpyran is a product formed from chlorophyll by an intramolecular change. E. W. W.

**Furfuraldehyde from Beetroots and Molasses.** By KARL ANTONIE. *Ber. chem. Ges.*, 1899, 32, 46. from *Zem. Zucker-Ind. Zösch.*, 28, 155—157. —The colour of the furfuraldehyde-phloroglucinol obtained from molasses is not the same as that of the pure compound. In an experiment in which large quantities were employed, about 7 per cent. of a substance which appeared to be methylfurfuraldehyde was found in the product which boiled at 160—165°. E. W. W.

**Constitution of Arginine.** By ERNST SCHWABE and ERNST WINTERSTEIN. *Ber. chem. Ges.*, 32, 5131—5134. Compare *Abstr.*, 1898, 1, 181, 1898, 1, 117. —The formula previously proposed by the authors for arginine is modified by the fact that this substance is formed when cyanine is treated in the cold with cyanamide. Ornithine itself is probably di-hydrocyanic acid, since the distillation of its hydrochloride yields a small amount of a substance which gives the reaction of pyridine, but has not yet been analysed. A. H.

**Benzylic Compounds of Hetero Bases.** By D. LAWSON. *Zell. physiol. Chem.*, 1899, 28, 151—156. —A method is described of isolating the hetero bases by the use of benzylic chloride and subsequent extraction with various solvents such as light petroleum. W. I. H.

**An Alkaloid contained in the Bark of the Pomegranate.** By AUGUST FRIEDBERG. *Monatsh.*, 1899, 29, 551—555. —From the light petroleum mother liquors obtained in the preparation of methylpomegranate from the pomegranate root an oily substance may be separated from which the author has isolated a base of the composition  $C_{17}H_{17}N$ . In decomposing the picrate by means of potassium carbonate it is obtained as a colourless oil which has a very faint basic odour and boils at 114—115° under 14 mm. pressure. It is soluble in water in all proportions, giving a strongly alkaline solution. The picrate,  $C_{17}H_{17}N$ , forms a crystalline powder melting at 155—156° and soluble in benzene, alcohol. The picnate,  $C_{17}H_{17}N.HANCO_3$ , separates from dilute hydrochloric acid in orange-yellow crystals and melts at 111—112°. The hydrochloride is a viscous mass soluble in water.

The base forms a salt with carbonic acid,  $C_{17}H_{17}N$ , which separates from

water in large, colourless, lustrous crystals which melt at  $100^{\circ}$  and dissolve in alcohol, but are insoluble in ether. The  $\beta$  hydrochloride,  $C_4H_9ON_2.HCl$ , crystallises from dilute alcohol in slender, colourless needles which melt with decomposition and evolution of gas at  $205^{\circ}$  and are very soluble in water but insoluble in absolute alcohol; the aqueous solution of the hydrochloride gives a yellow, oily precipitate with a solution of gold chloride. T. H. P.

**Abnormal Aurichlorides of Organic Bases.** By GOTTFRIED FENNER and JULIUS TAFEL (*Ber.*, 1893, 32, 3613—3618. Compare Abstr., 1895, i, 446).—The normal aurichloride of piperidine is always formed when auric chloride acts on piperidine hydrochloride in aqueous solution, and is also produced by the action of water on the abnormal salt. The latter is formed when piperidine hydrochloride and auric chloride are brought together in alcoholic solution, or when the normal salt is treated in alcoholic solution with hydrogen chloride or piperidine hydrochloride. It appears to dissociate when heated, either alone or in alcoholic solution, into the normal salt and piperidine hydrochloride. *Abnormal isopropylamine aurichloride*,  $C_3H_7N.AuCl_4$ , is prepared in a similar manner to the piperidine compound, and is a golden-yellow, microcrystalline powder melting at  $150^{\circ}$ ; water decomposes it with formation of the normal salt. *Abnormal 1-ethylpiperidine aurichloride*,  $C_5H_{11}N.AuCl_4$ , melts between  $80$  and  $85^{\circ}$  and yields the normal salt when treated with water. In aqueous solution, 2:5-dimethylpyrrolidine yields an oily normal aurichloride, but in alcoholic solution an *abnormal aurichloride*, which crystallises in yellow plates melting at  $102$ — $104^{\circ}$ . *Abnormal piperidine aurichloride* melts at  $150^{\circ}$  and decomposes at  $260^{\circ}$ .

Methylamine, confine, aniline, and pyridine do not appear to yield abnormal salts. A. H.

**Synthesis of Glutaric and Trimethylene Derivatives.** By LILIO GUARESCHI and ERNESTO GRANDE (*Chim. Centr.*, 1903, ii, 439—440; from *Atti. Acad. Sc. Torino*, 34. Compare Abstr., 1903, 33).—3:5-Diciano-4-ethyl-1:4-dithio-trimethylenediamine dithiocarbamate

*homocaronamide*,  $NH\langle\begin{smallmatrix} CO \cdot C \cdot CN \\ CO \cdot C \cdot CN \end{smallmatrix}\rangle CMeEt$ , prepared from the di-

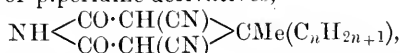
bromide,  $NH\langle\begin{smallmatrix} CO \cdot CBr \cdot CN \\ C \cdot CBr \cdot CN \end{smallmatrix}\rangle CMeEt$ , by heating at  $110^{\circ}$  for a

short time, crystallises in hard, lustrous, rhombic prisms, melts at  $210^{\circ}$ , and is slightly soluble in water. When heated with sodium hydroxide, the imide loses 1 mol. of ammonia, and the solution, after acidifying with acetic acid, forms a silver salt; when treated with silver nitrate, by the action of hydrogen sulphide on this salt, an acid is obtained which is soluble in water and melts at  $184^{\circ}$ . Unlike diuran-2:6-dioxy-4-methyl-4-ethylpiperidine, the dicarbonyl imide does not evolve ethane from neutral aqueous solutions, and even when heated to  $240$ — $245^{\circ}$  gives only small quantities of carbon monoxide, methane, and ethane. The ammonium derivative of 3:5-di-ciano-2-ethyl-4-dimethylpiperidine, prepared by the action of acetone on ethyl cyanoacetate in presence of alcoholic ammonia, forms a white, crystalline, easily soluble mass; its aqueous solution does not evolve gas even if

left for several days. The base,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{CN}) \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} > \text{CMe}_2$ , crystallises in lustrous, colourless leaflets, melts at  $216-217^\circ$ , and is slightly soluble in cold water, more so in alcohol or acetic acid. With potassium nitrite and sulphuric acid, it gives a characteristic, yellow coloration, and when heated at  $310-320^\circ$  evolves methane. The *silver* derivative,  $\text{C}_9\text{H}_5\text{O}_2\text{N}_3\text{Ag}$ , forms a white, crystalline precipitate. The *dibromo*-derivative,  $\text{C}_9\text{H}_7\text{O}_2\text{N}_3\text{Br}_2$ , melts at  $190-195^\circ$ , and when heated for a long time with a 40 per cent. solution of acetic acid yields 3 : 5-dicyano-4-dimethyltrimethylenedicarbonimide,  $\text{C}_9\text{H}_7\text{O}_2\text{N}_3$ , which crystallises in small, hard, lustrous, colourless prisms, melts and decomposes at  $242^\circ$ , is soluble in water, alcohol, or acetic acid, and forms a silver salt. 3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-hexylpiperidine, prepared by the action of methyl hexyl ketone on ethyl cyanoacetate in presence of alcoholic ammonia, crystallises in broad, colourless leaflets, melts at  $156-157^\circ$ , is very slightly soluble in water, and decomposes in aqueous solutions, forming hexane and dicyanomethylglutaconimide,  $\text{C}_8\text{H}_5\text{O}_2\text{N}_3$ . The *dibromo*-derivative,  $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3\text{Br}_2$ , forms small, lustrous crystals, melts at  $135^\circ$ , loses its bromine when heated for several hours with a 50 per cent. solution of acetic acid, forming 3 : 5-dicyano-4-methyl-4-hexyltrimethylenedicarbonimide,  $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3$ ; this compound crystallises in nacreous leaflets, melts at  $154-155^\circ$ , and is very slightly soluble in water.

Pinacoline does not react with ethyl cyanoacetate and ammonia.

The following conclusions are drawn: (1) By the action of ethyl cyanoacetate and ammonia on ketones of the type  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_n\text{H}_{2n+1}$ , the glutarimides or piperidine derivatives,



are formed. These compounds may also be regarded as derivatives of *aa*-dicyanoglutaric acids,  $\text{C}_n\text{H}_{2n+1} \cdot \text{CMe}[\text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}]_2$ . (2) These new saturated compounds form dibromo-derivatives from which tri-

methylene derivatives,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{C}(\text{CN}) \\ \text{CO} \cdot \text{C}(\text{CN}) \end{smallmatrix} > \text{CMe}(\text{C}_n\text{H}_{2n+1})$ , may be prepared. Unlike the compounds of the preceding class, these substances, and the dibromo-derivatives from which they are prepared, do not give a yellow coloration with potassium nitrite and sulphuric acid.

E. W. W.

**Action of Heat on Hydrogenised Compounds.** By ILLIO GUARESCHI and ERNESTO GRANDE (*Chem. Centr.*, 1899, ii, 440; from *Atti Real. Accad. Torino*, 34. Compare this vol., i, 52).—(1) Cyano-trimethyldihydropyridone,  $\text{C}_9\text{H}_{12}\text{ON}_2$ , decomposes at  $320-330^\circ$ , forming mainly methane and cyanodimethylpyridone, which melts at  $288-289^\circ$ . (2) Cyanotetramethyldihydropyridone,  $\text{C}_{10}\text{H}_{14}\text{ON}_2$ , which melts at  $142-143.5^\circ$ , decomposes at  $320-330^\circ$ , forming methane and cyano-1 : (?)dimethylpyridone,  $\text{C}_9\text{H}_{10}\text{ON}_2$ ; the latter melts at  $203-204^\circ$ . 3 : 5-Dicyano-2 : 6-dioxy-4-dimethylpiperidine, and other compounds which contain the group  $\cdot\text{CH}_2 \cdot \text{CMeEt} \cdot$  or the group  $\cdot\text{CH}_2 \cdot \text{CMe}_2 \cdot$ , under similar conditions, yield methane or ethane. (3) Ethyl 2 : 4 : 6-trimethyldihydropyridinedicarboxylate,  $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}$ , decomposes at

340—350°, forming carbon dioxide, carbon monoxide, methane, ethylene, and alcohol, together with ethyl 2:6-dimethylpyridine-5-carboxylate,  $C_{10}H_{13}O_2N$ , and ethyl 2:6-dimethylpyridinedicarboxylate. Of these two esters, the former (compare Weiss, Abstr., 1886, 719) is a colourless base and boils at 255—257°, and the latter crystallises in long, colourless needles, melts at 73°, and boils at 300—305°. (4) Ethyl phenyldimethyldihydropyridinedicarboxylate,  $C_{19}H_{23}O_4N$ , prepared by the action of benzaldehyde on ethyl acetoacetate in presence of alcoholic ammonia, forms crystals and melts at 157°. On dry distillation, it decomposes into carbon dioxide, ethylene, hydrogen, and ethyl phenyldimethylpyridinecarboxylate,  $C_{16}H_{17}O_2N$ , which boils at 315—320°. Alcohol, benzene, carbon monoxide, and ethyl trimethylpyridinedicarboxylate are also formed by secondary reactions. (5) Ethyl dimethyldihydropyridinedicarboxylate,  $C_{13}H_{19}O_4N$ , prepared by the action of formaldehyde on ethyl acetoacetate in presence of alcoholic ammonia, crystallises in fluorescent needles, melts at 183°, and, on dry distillation under the ordinary pressure yields carbon monoxide, carbon dioxide, ethylene, ethane (?), ethyl dimethylpyridinecarboxylate, and ethyl dimethylpyridinedicarboxylate. The last compound melts at 73°, and is the principal product of the decomposition.

The results of these experiments show that the esters of dihydroacids decompose on distillation, liberating 1 mol. of hydrogen, which often takes part in secondary reducing actions, and that the carboxy-ethyl group of the original compound, or of the ester derived from it, also decomposes, forming carbon dioxide and ethylene.

E. W. W.

**Pseudo-ammonium Bases.** By ARTHUR HANTZSCH and M. KALB (*Ber.*, 1899, 32, 3109—3131. Compare Abstr., 1899, i, 400).—Pseudo-bases are neutral substances isomeric with true ammonium hydroxide bases, and correspond with the pseudo-acids previously described (Abstr., 1899, i, 399; this vol., i, 94, 103). Their existence may be discovered (1) by the phenomenon of gradual neutralisation, when the conductivity of a mixture of the ammonium chloride with sodium hydroxide gradually decreases to that of the sodium chloride produced, as the true base changes to the pseudo-base; (2) by 'abnormal neutralisation phenomena,' even where the velocity of change in (1) is too great to be observed, the neutral ammonium chloride giving a neutral solution with an equivalent of alkali, and the neutral pseudo-base giving a neutral salt when mixed with an equivalent of acid; (3) by the reluctance of the dry pseudo-base to combine with a dry acid or anhydride ( $CO_2, HCN$ ); (4) by the formation of abnormal anhydrides and ethers.

The ammonium cyanides resemble the hydroxides, and frequently pass into *pseudo*-salts which are insoluble in water, soluble in organic solvents, undissociated, and stable towards acids.

Methylpyridinium hydroxide,  $C_5NH_5Me(OH)$ , gave  $\mu_{32} = 213$  and  $\mu_{25.6} = 219$  at 25; it is almost completely dissociated at moderate dilution and shows no tendency to pass into a pseudo-base.

1-Methylquinolinium 1-hydroxide,  $C_9NH_7Me(OH)$ , gave  $\mu_{32} = 207.5$ ,

but is much less stable than the pyridine base, and passes into 1-methyl-1 : 2 dihydroquinoline oxide,  $O(C_9NH_7Me)_2$ , the anhydride of the pseudo-base; this separates in minute, white needles.

Methylisoquinolinium hydroxide gave  $\mu_{32} = 206.9$ , and, like the preceding base, rapidly undergoes change.

Phenylmethyleridinium hydroxide,  $CPh \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} NMe \cdot OH$ , gave

$\mu_{256} = 117.5$  at  $0^\circ$ , falling to  $57.4$  in 10 minutes,  $14.1$  in 1 hour, and becoming zero in about 15 hours. For the chloride,  $\mu_{128} = 45.6$  at  $0^\circ$ , and  $\mu_{20}$  is calculated to be  $50.0$ ; whence  $\mu_{20}$  for the base =  $127.2$ , showing that it is as highly dissociated as the caustic alkalis. At  $25^\circ$ , the isomeric change proceeds very rapidly, especially during the first few seconds, and is complete within 6 hours. Phenylmethyleridol,

$OH \cdot CPh \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} NMe$ , the pseudo-base, is completely insoluble in water, to which it imparts not the slightest conductivity, and does not combine with carbon dioxide or hydrogen cyanide, although with strong acids it gives true acridinium salts; it is stable towards oxidising and reducing agents, and cannot therefore be represented by the formula  $CHPh \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} NMe \cdot O$ .

When liberated from the iodide by sodium hydroxide, dimethyl-

acridinium hydroxide,  $CMe \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} NMe \cdot OH$ , is completely converted

into the pseudo-base in 3 hours at  $0^\circ$  in  $N/512$  solution and methylacridinium hydroxide within 20 minutes in  $N/256$  solution. At  $25^\circ$ , 'gradual neutralisation' can no longer be observed, but 'abnormal neutralisation' occurs, the neutral iodides giving a neutral solution on adding an equivalent of caustic soda, whilst the pseudo-base is precipitated immediately, a separation which only takes place very slowly in the case of the phenylmethyleridinium base.

Phenylmethyleridine cyanide,  $NMe \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} CPh \cdot CN$ , separates gradually from a mixture of potassium cyanide and phenylmethyleridinium iodide as a white, crystalline substance, which melts at  $176^\circ$ , dissolves in organic solvents but not in water, and is not attacked by acids. The first product is the true cyanide,

$CPh \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} NMe \cdot CN$ , which is stable at  $0^\circ$ , but is gradually converted into the 'pseudo-salt' at  $25^\circ$ , the conductivity reaching a minimum within 16 hours. The pseudo-base does not combine with hydrogen cyanide.

The azonium bases are regarded as pseudo-bases and show 'abnormal neutralisation' phenomena; thus the neutral salt  $N \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} NPh \cdot Cl$  at once gives a neutral solution with an



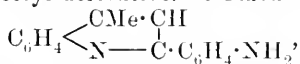
equivalent of caustic soda and is converted into the pseudo-base  $\text{N}^+\cdot\text{C}_6\text{H}_4\cdot\text{NPh}$   
 $\text{CPh}=\text{CPh}\cdot\text{OH}$ , which is quite insoluble in water, but dissolves in organic solvents.

Aqueous solutions of cotarnine give evidence of the presence of a pseudo-base in the high temperature coefficient of the dissociation-constant and the formula  $\text{C}_8\text{H}_6\text{O}_3\langle\text{CH}(\text{OH})\rangle\text{NMe}$  is suggested for *pseudocotarnine*. By the action of hydrogen cyanide on cotarnine, or of potassium cyanide on the hydrochloride, a cyanide is produced which is regarded as *pseudocotarninecyanide*,  $\text{C}_8\text{H}_6\text{O}_3\langle\text{CH}(\text{CN})\rangle\text{NMe}$ ; it melts at  $86^\circ$ , dissolves readily in organic solvents but only slightly in cold water, crystallises unchanged from water, and, unlike the true cyanides, is neutral, undissociated, indifferent to hydrochloric acid, and gives no precipitate with silver nitrate. T. M. L.

**Synthesis of 2- and 4-Hydroxyquinolines.** By RUDOLF CAMPS (*Ber.*, 1899, 32, 3228—3234).—*o*-Acetaminoacetophenone is readily converted by aqueous soda into a mixture of 2-hydroxy-4-methylquinoline and 4-hydroxy-2-methylquinoline, the elements of water being eliminated.

A similar reaction is given by other acylaminoacetophenones, 2- or 4-hydroxy-derivatives, or a mixture of these, being formed, according to the constitution of the acid residues.

In addition to the two hydroxymethylquinolines, *o*-acetaminoacetophenone yields a small amount of *o*-aminoacetophenone and of *o*-flavaniline and its acetyl derivative. *o*-Flavaniline,



which has already been obtained in very small amount by Bischler (*Abstr.*, 1893, i, 531), crystallises in yellow needles melting at  $83\text{--}84^\circ$ , the *acetyl* derivative melts at  $138^\circ$ .

In the preparation of *o*-aminoacetophenone by the reduction of the corresponding nitro-compound, an oil boiling at  $127\text{--}128^\circ$  under 16 mm. pressure is obtained, which yields indigo when heated in the air. Its constitution has not yet been ascertained. A. II.

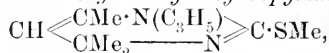
**Carbamide and Thiocarbamide Derivatives of Diacetone-amine.** By WILHELM TRAUBE and H. W. F. LORENZ (*Ber.*, 1899, 32, 3156—3163. Compare *Abstr.*, 1894, i, 170).—Anhydrosdiacetone-phenylthiocarbamide may be represented by one or other of the following formulæ:  $\text{CH}\langle\text{CMe}\cdot\text{S}\rangle\text{C}\cdot\text{NHPh}$  or  $\text{CH}\langle\text{CMe}\cdot\text{NPh}\rangle\text{C}\cdot\text{SH}$ ; in accordance with the former, it should, as a derivative of penthi-azoline, have a basic character, whereas it reacts as a feeble acid forming metallic derivatives, the *silver* compound,  $\text{C}_{13}\text{H}_{15}\text{N}_2\text{SAg}$ , being described; the chemical behaviour of the substance is therefore more closely indicated by the second formula. The basic character of the pyrimidine ring is rendered manifest when the compound is alkylated the methyl derivative being a strong base.

The *oxime*,  $C_{13}H_9ON_3S$ , of diacetonephenylthiocarbamide, obtained by treating this compound with alcoholic hydroxylamine, melts at  $152-153^\circ$ ; the corresponding *phenylhydrazone*,  $C_{19}H_{24}N_4S$ , separates from alcohol in colourless crystals and melts at  $169^\circ$ .

*2-Methothio-1-phenyl-4:4:6-trimethyldihydropyrimidine hydriodide*,  $C_{14}H_{18}N_2S \cdot HI$ , produced by mixing together alcoholic solutions of anhydrothiodiacetonephenylthiocarbamide and methyl iodide, separates from water in lustrous crystals.

*Diacetoneallylthiocarbamide*,  $C_{10}H_{18}ON_2S$ , crystallises from alcohol and melts at  $138^\circ$ ; its *phenylhydrazone* melts at  $122^\circ$ . The *anhydro*-compound is obtained either by heating the thiocarbamide above its melting point, or by treating it with warm dilute sulphuric acid; it crystallises from alcohol and melts at  $130^\circ$ ; its *silver* derivative is produced by treating the substance with an alcoholic solution of ammonia and silver nitrate.

*2-Methothio-4:4:6-trimethyl-1-allyldihydropyrimidine*,



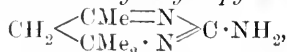
obtained as an oily base by treating anhydrodiacetoneallylthiocarbamide with an alcoholic solution of methyl iodide and sodium methoxide, boils at  $159^\circ$  under a pressure of 580 mm.; its *platinichloride*,  $(C_{11}H_{18}N_2S)_2 \cdot H_2PtCl_6$ , forms orange-yellow crystals.

Anhydrodiacetonecarbamide (Abstr., *loc. cit.*) resembles the preceding anhydrothiocarbamides, and by analogy its formula should be  $CH \begin{array}{c} \diagup CMe \cdot NH \\ \diagdown CMe_2 \end{array} \text{---} NH \cdot CO$ .

*Trinitroanhydrodiacetonecarbamide*,  $C_7H_9ON_2(NO_2)_3$ , crystallises from methyl alcohol in colourless, silky needles which, when heated, take fire like guncotton. The substance is a dibasic acid dissolving in alkalis and ammonia to form dark yellow solutions. The *barium* salt,  $C_7H_7N_2(NO_2)_3Ba + 3H_2O$ , crystallises in reddish-yellow needles; when heated, it explodes violently, and is decomposed by prolonged boiling with water. The *silver* salt, obtained in brown needles, is even more explosive.

The free acid, when boiled for some time with water, is converted into the compound  $C_6H_9O_4N_3$ ; this substance, which is obtained by concentrating the solution under diminished pressure, crystallises in obliquely truncated prisms and melts at  $214^\circ$ ; it is a monobasic acid, and is not explosive; its *barium* salt,  $(C_6H_8O_4N_3)_2Ba + 2H_2O$ , is sparingly soluble in water. G. T. M.

**Action of Amidines on Mesityl Oxide and Phorone.** By WILHELM TRAUBE and RUDOLF SCHWARZ (*Ber.*, 3163—3174. Compare Abstr., 1887, 932; 1894, i, 170; 1898, i, 121; and preceding abstract).—*2-Amino-4:4:6-trimethyldihydropyrimidine*,



prepared by heating a mixture of guanidine and mesityl oxide on the water-bath, crystallises from hot water in white, rhombic plates, melts at  $145^\circ$ , boils at  $210^\circ$  under a pressure of 10 mm., and sublimes in a vacuum, forming fern-like aggregates of slender needles. It

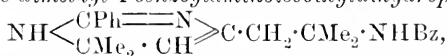
dissolves in water, alcohol, or benzene, and rapidly absorbs carbon dioxide from the air; it is a strong monoacidic base, its salts being decomposed by caustic alkalis but not by ammonia. The hydrochloride is very hygroscopic, the *oxalate* forms colourless crystals and melts at  $238^{\circ}$ , the *picrate* crystallises in needles and melts at  $246^{\circ}$ , and the *platinichloride*,  $(C_7H_{13}N_2)_2 \cdot H_2PtCl_6$ , and *mercurichloride* melt at  $176-177^{\circ}$  and  $184^{\circ}$  respectively. The base takes up six atoms of bromine when treated with this reagent in glacial acetic acid solution; the product, when crystallised from warm water, forms reddish-purple, four-sided prisms which sinter together at  $108^{\circ}$  and melt at  $113^{\circ}$ ; when separating from boiling solutions, it appears as yellow needles, these sinter together at  $108^{\circ}$  but only melt at  $137^{\circ}$ ; the purple prisms appear to be an impure form (containing free bromine) of the yellow compound,  $C_7H_{14}N_3Br_6$ ; the latter compound is decomposed on prolonged boiling with water. When aminotrimethyldihydropyrimidine is heated with acetic anhydride, it yields an oily *acetyl* derivative which has basic characters; its *platinichloride*,  $(C_9H_{15}ON_3)_2 \cdot H_2PtCl_6$ , crystallises in yellow leaflets and melts at  $181-182^{\circ}$ .

*Diacetoneguanidine*,  $NH \cdot C(NH_2) \cdot NH \cdot CMe_2 \cdot CH_2Ac$ , prepared by heating a mixture of guanidine thiocyanate, mesityl oxide, and sodium ethoxide at  $120^{\circ}$ , crystallises from hot water in needles melting at  $163^{\circ}$ ; it was only obtained crystalline in one experiment, the product at other times being amorphous. The *acetyl* derivative,  $C_9H_{17}O_2N_3$ , produced by heating the crude base with acetic anhydride, crystallises from hot water in long needles and melts at  $157^{\circ}$ .

*2-Phenyl-4:4:6-trimethyldihydropyrimidine* (anhydrodiacetonebenzamidine),  $CH_2 \begin{smallmatrix} <CMe_2 \cdot N \\ <CMe_2 \cdot N \end{smallmatrix} >CPh$ , obtained by heating benzamide and mesityl oxide on the water-bath, separates from methyl alcohol in colourless, acicular prisms and melts at  $91^{\circ}$ ; it is readily soluble in the ordinary organic solvents. The *hydrochloride*,  $C_{13}H_{16}N_2 \cdot HCl + 2H_2O$ , crystallises from alcohol in well-defined cubes and melts at  $74^{\circ}$ ; the *platinichloride*,  $(C_{13}H_{16}N_2)_2 \cdot H_2PtCl_6 + 2H_2O$ , crystallises in aggregates of rhombic plates and melts at  $193^{\circ}$ ; the *mercurichloride*,  $C_{13}H_{16}N_2 \cdot HgCl_2 + 2H_2O$ , crystallises in flattened needles melting at  $179^{\circ}$ ; the *oxalate* crystallises in rosettes of leaflets and melts at  $210-211^{\circ}$ . *Anhydrotriacetonediguandine*,  $C_{11}H_{22}N_6$ , results from the condensation of guanidine (2 mols.) with phorone (1 mol.), the reaction being assisted by heating on the water-bath; the product, a diacidic base, crystallises from water in long needles melting at  $171-175^{\circ}$ . The *hydrochloride*,  $C_{11}H_{22}N_6 \cdot 2HCl$ , crystallises in lustrous, rhombic plates and melts at  $269^{\circ}$ ; the *platinichloride*,  $C_{11}H_{22}N_6 \cdot H_2PtCl_6 + H_2O$ , crystallises in yellow leaflets and decomposes at  $246^{\circ}$ . *Triacetonedibenzamidine*,  $CO(CH_2 \cdot CMe_2 \cdot NH \cdot CPh \cdot NH)_2$ , obtained by heating together phorone and benzamidine and extracting the product with cold alcohol, crystallises from the alcoholic solution on the addition of light petroleum; it melts at  $160^{\circ}$ . The *nitrate* crystallises in prisms or six-sided plates; when separated slowly from warm water, it melts at  $134^{\circ}$ , but when repeatedly crystallised from rapidly cooled solutions, it melts at  $218^{\circ}$ . The *platinichloride*,  $C_{23}H_{30}ON_4 \cdot H_2PtCl_6 + H_2O$

crystallises from hot water in four-sided leaflets and decomposes at  $263\text{--}265^\circ$ ; the mercurichloride melts at  $269^\circ$ .

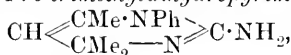
2-Phenyl-6 : 6-dimethyl 4-benzoylaminoisobutylidihydropyrimidine,



formed as a bye-product in the preceding condensation, is obtained in larger quantity when the reaction is carried out at  $160\text{--}170^\circ$ , or when the preceding base is heated to the same temperature; it crystallises from alcohol in four-sided, acicular prisms, and melts at  $212^\circ$ , sintering at  $201^\circ$ . The hydrochloride,  $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O} \cdot \text{HCl} + \text{H}_2\text{O}$ , crystallises from hot water in six-sided prisms, sinters at  $150^\circ$ , and melts at  $165^\circ$ . G. T. M.

**Carbamide and Guanidine Derivatives of Diacetoneamine.** By WILHELM TRAUBE and MAX SCHALL (*Ber.*, 1899, 32, 3174—3176. Compare preceding abstracts).—The cyclic anhydrodiacetonephenylthiocarbamide does not exchange its sulphur for oxygen, but the open chain diacetonephenylthiocarbamide, when boiled with yellow mercuric oxide and alcohol, yields an oil which is probably diacetonephenylcarbamide, for on further treatment with acetic acid 2-hydroxy-1-phenyl-4 : 4 : 6-trimethyldihydropyrimidine (anhydrodiacetonephenylcarbamide),  $\text{CH} \begin{array}{c} \text{CMe} \cdot \text{NPh} \\ \text{CMe}_2 - \text{N} \end{array} \text{C} \cdot \text{OH}$ , is produced; this substance crystallises from dilute alcohol in lustrous leaflets, melts at  $161^\circ$ , and dissolves in concentrated, but not in dilute, acids.

2-Amino-1-phenyl-4 : 4 : 6-trimethyldihydropyrimidine,



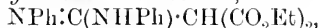
results when the removal of sulphur is effected by mercuric oxide in alcoholic ammonia; it melts at  $161^\circ$  and is a strong base, but its salts are ill-defined; the platinichloride, however, is crystalline.

Diacetone $\alpha$ -tolylthiocarbamide melts at  $168^\circ$ ; when treated in succession with mercuric oxide and acetic acid, it yields 2-hydroxy-1-tolyl-4 : 4 : 6-trimethyldihydropyrimidine, which crystallises from dilute alcohol in needles melting at  $151^\circ$ .

Similar compounds are obtained with xylilearbimide. G. T. M.

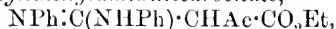
**Additive Products of the Carbodiimides.** By WILHELM TRAUBE and A. EYME (*Ber.*, 1899, 32, 3176—3178. Compare Abstr., 1898, i, 241, and 1899, i, 192).—The carbodiimides readily combine with ethyl malonate, ethyl acetoacetate, and similar substances in the presence of a trace of sodium ethoxide, yielding additive products having the general formula  $\text{NR} : \text{C} : \text{NHR} \cdot \text{CHXY}$ .

Ethyl diphenylethenylamidinedecarbonate,



produced from carbodiphenylimide and ethyl malonate, crystallises in colourless needles and melts at  $167^\circ$ . The corresponding ditolyl compound from carboditolylimide melts at  $125^\circ$ .

Ethyl acetyldiphenylethenylamidinedecarbonate,



from ethyl acetoacetate and carbodiphenylimide, melts at  $109^\circ$ ; the ditolyl compound melts at  $97^\circ$ .

*Diacetyldiphenylethenylamidine*,  $\text{NPh}\cdot\text{C}(\text{NHPh})\cdot\text{CHAc}_2$ , from acetylacetone and carbodiphenylimide, melts at  $150^\circ$ ; the *ditolyl* compound melts at  $149^\circ$ . The combination does not take place unless sodium ethoxide is present; all the compounds produced are readily soluble in the ordinary organic solvents. G. T. M.

**Preparation of Phenylindoxyl.** By MARTIN HENZE (*Ber.*, 1899, 32, 3055—3060. Compare Abstr., 1895, i, 371, and 1896, i, 696).—The following compounds were prepared in attempting to synthesise phenylindoxyl.

*Phenyliminodiphenylacetic acid*,  $\text{NPh}(\text{CHPh}\cdot\text{CO}_2\text{H})_2$ , produced either by melting together ethyl anilinophenylacetate and zinc chloride or by warming a mixture of anilinophenylacetic and bromophenylacetic acids at  $100^\circ$ , is a white, amorphous powder sintering at  $90^\circ$  and melting at  $105\text{--}110^\circ$ .

*Tetraphenyl- $\beta\delta$ -diketopiperazine*,  $\text{CHPh}\langle\text{NPh}\cdot\text{CO}\rangle\text{CHPh}$ , obtained by heating a solution of anilinophenylacetic acid in acetic anhydride at  $155^\circ$ , is a white powder decomposing at  $260^\circ$ ; this reaction is reversed when the condensation product is boiled with sodium amyloxide.

*Ethyl anthranilphenylacetate*, prepared by boiling an alcoholic solution of anthranilic acid, ethyl bromophenylacetate, and sodium acetate, crystallises in white needles and melts at  $175\text{--}176^\circ$ , the *acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , melts at  $227^\circ$ . Neither this acid nor benzylanthranilic acid is affected by fusion with caustic alkalis at  $209\text{--}300^\circ$ . G. T. M.

**Orthoquinonoid Structure of Saffranine, Oxazine, and Thiazine Colouring Matters.** By ARTHUR G. GREEN (*Ber.*, 1899, 32, 3155—3156. Compare Kehrman, this vol., i, 62).—With reference to Kehrman's formulation of the azonium, oxazine, and thiazine colours as orthoquinonoid bases, it is pointed out that the author had previously expressed similar views (*Proc.*, 1892, 195, and 1896, 226), and had also given reasons for believing that oxygen and sulphur are quadrivalent in the latter compounds. The following are suggested as alternative formulæ,  $\text{C}_6\text{H}_4\langle\text{NCl}\rangle\text{C}_6\text{H}_4$  and

$\text{C}_6\text{H}_4\langle\text{NCl}\rangle\text{O}\text{—}\text{C}_6\text{H}_4$ . These formulæ differ from those proposed by Kehrman,  $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{OC}\text{—}\text{C}_6\text{H}_4$ , in containing the acidic radicle (chlorine in this case) attached to nitrogen and not to oxygen (or sulphur); this seems more probable in view of the more basic character of the nitrogen atom.

Another constitution for these substances is possible, namely, that in which both aromatic nuclei are represented as being quinonoid,  $\text{C}_6\text{H}_4\langle\text{NCl}\rangle\text{C}_6\text{H}_4$  and  $\text{C}_6\text{H}_4\langle\text{NCl}\rangle\text{O}\text{=}\text{C}_6\text{H}_4$ . In certain azonium compounds, it is found that both nuclei appear to be quinonoid, and react with amines; these formulæ offer a simple explanation of this behaviour, it being otherwise necessary to assume a migration of the

quinone linkings (Kehrmann, *Abstr.*, 1898, i, 439). Moreover, the formulæ suggested for the azonium bases render it possible to represent saffranones, rosindones, and similar anhydrides as *p*-anhydro-

compounds;  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{N} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{R} > \text{C}_6\text{H}_4$  or  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{N} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{R} \equiv \text{C}_6\text{H}_4$ , this view of

their constitution being more probable than that based on Kehrmann's

formula, which represents them as *m*-anhydrides,  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{N} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{R} > \text{C}_6\text{H}_4$ .

G. T. M.

**Constitution of  $\delta$ -Methyluric Acid.** By ROBERT BEHREND and EMIL DIETRICH (*Annalen*, 1899, 309, 260—281).—Although uric acid contains only four replaceable atoms of hydrogen, five methyluric acids have been described (compare E. Fischer, *Ber.*, 1899, 32, 461). Of these compounds,  $\delta$ -methyluric acid, which certainly contains the methyl radicle in the alloxan group, is regarded by Fischer as 4-methyl-

uric acid,  $\text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{NH} > \text{CO}$ , along with  $\alpha$ -methyluric acid (Hill) and  $\zeta$ -methyluric acid (Fischer and Ach, this vol., i, 63). The authors' experiments, however, lead them to the conclusion that  $\delta$ -methyluric

acid is 6-methyluric acid,  $\text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{NH} > \text{CO}$ . If this is actually

the case, it would become necessary to reconsider the accepted formulæ of several purine derivatives. The results which have led to this conclusion are as follows. Besides acetylcarbamide and oxalic acid, methyluracil yields oxaluric and acetic acids when oxidised with potassium permanganate. In the same circumstances,  $\beta$ -dimethyluracil gives rise to acetylmethylcarbamide, and acetic, oxalic, and methyloxaluric acids; from  $\alpha$ -dimethyluracil, methyloxaluric acid only is obtained, showing that the isomerides, so far as concerns the position of the methyl group, have the constitution  $\text{NMe} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CO} \cdot \text{CH} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{CO} \cdot \text{NH} > \text{CMe}$ .

Nitric acid converts  $\alpha$ -dimethyluracil into nitromethyluracilcarboxylic acid,  $\text{NMe} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CO} \cdot \text{C}(\text{NO}_2) \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , which loses carbon dioxide, yielding methylnitrouracil; the same methylnitrouracil is produced by methylating nitrouracil; it is the same substance from which von Loeben first prepared  $\delta$ -methyluric acid.

*$\beta$ -Dimethyluracil*,  $\text{NMe} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{CO} \cdot \text{CH} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{CO} \cdot \text{NH} > \text{CMe}$ , occurring in the mother liquor of  $\alpha$ -dimethyluracil (m. p. 219—220°), is produced when methyluracil, dissolved in alcoholic potash, is heated with methyl iodide,  $\alpha$ -dimethyluracil and trimethyluracil being formed at the same time; it crystallises in serrated leaflets or long needles before precipitation, the purified substance forming lustrous prisms which melt at 260°.

*Methyloxaluric acid*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , prepared by oxidising  $\alpha$ -dimethyluracil, crystallises from water in prisms, and melts and decomposes at 180—190°, according to the rate at which the tempera-

ture rises; the *potassium* salt forms a gelatinous mass which becomes crystalline.

*Nitromethyluracilcarboxylic acid*, obtained by the action of nitric and sulphuric acids on  $\alpha$ -dimethyluracil, crystallises from water in needles or prisms containing the solvent, which is removed at  $105^\circ$ , the anhydrous substance melting at  $255\text{--}256^\circ$ ; the *potassium* salt contains  $\text{H}_2\text{O}$ , and forms a *potassium nitrate* double salt.

Isodialuric acid is readily converted into dialuric acid under certain conditions, and if the analogous change took place when methylisodialuric acid is condensed with carbamide, 3-methyluric acid would be produced; the authors find, however, that dialuric acid itself yields no trace of uric acid, but merely undergoes, in part, oxidation to alloxan.

M. O. F.

**Deoxytheobromine.** By JULIUS TAFEL (*Ber.*, 1899, 32, 3194—3206. Compare the following abstract).—When a solution of theobromine in 50 per cent. sulphuric acid is submitted to electrolytic reduction, *deoxytheobromine* (5-oxy-1:4-dimethyl-6:7-dihydro-purine),  $\text{NH}\cdot\text{CH}_2\cdot\overset{\text{||}}{\underset{\text{||}}{\text{C}}}\cdot\text{NMe}$   
 $\text{CO}\cdot\text{NMe}\cdot\overset{\text{||}}{\underset{\text{||}}{\text{C}}}\text{—N}\geq\text{CH}$ , is formed; it crystallises from water in thin prisms containing  $2\text{H}_2\text{O}$ , which are sparingly soluble in cold, but very readily in boiling water; the anhydrous base melts at  $215^\circ$ . The *hydrochloride* forms large, very soluble prisms, the *platinichloride* is a granular precipitate, the *picrate* decomposes at  $205^\circ$ , and the *mercurichloride* is a crystalline precipitate. Bromine in chloroform solution converts the base into an unstable *monobromo*-compound,  $\text{C}_7\text{H}_9\text{O}_4\text{NBr}$ , which readily passes into the isomeric 5-oxy-1:4-dimethylpurine hydrobromide. Deoxytheobromine is converted by oxidation with silver acetate, bromine, and acetic acid, or lead peroxide and acetic acid into 5-oxy-1:4-dimethylpurine,  $\text{N}=\text{CH}\text{—}\overset{\text{||}}{\underset{\text{||}}{\text{C}}}\cdot\text{NMe}$   
 $\text{CO}\cdot\text{NMe}\cdot\overset{\text{||}}{\underset{\text{||}}{\text{C}}}\text{—N}\geq\text{CH}$ , which crystallises, with  $2\text{H}_2\text{O}$ , in colourless prisms, and melts, when anhydrous, at  $256\text{--}257^\circ$ . This compound is also formed by the methylation of 5-oxy-1-methylpurine, its constitution and that of deoxytheobromine being thus determined. The *hydrochloride*, *hydrobromide*, *hydrogen sulphate*, *picrate*, and *platinichloride* are all crystalline salts.

A. H.

**Deoxycaffeine.** By THOMAS B. BAILLIE and JULIUS TAFEL (*Ber.*, 1899, 32, 3206—3220. Compare Abstr., 1899, i, 268, and the preceding abstract).—In addition to the salts of deoxycaffeine which have already been described, the *sulphate*, *nitrate*, *cuprochloride*, and *methiodide* have been prepared. When boiled with baryta water, the base yields carbon dioxide, formic acid, an amino-acid of unknown composition, ammonia (1 mol.), and methylamine (2 mols.). Bromine in absence of water converts deoxycaffeine into a *monobromo*-compound which is probably 5-oxy-1:4-dimethylpurine 6-methobromide,  $\text{NMeBr}\cdot\text{CH}\cdot\overset{\text{||}}{\underset{\text{||}}{\text{C}}}\cdot\text{NMe}$   
 $\text{CO}\cdot\text{NMe}\cdot\overset{\text{||}}{\underset{\text{||}}{\text{C}}}\text{—N}\geq\text{CH}$ , whilst a yellow *perbromide* is formed when an excess of bromine is employed. Oxidation with lead peroxide and

acetic acid converts the base into *oxydimethylpurine methoacetate*,  

$$\text{NMeAc} \cdot \text{CH} \cdot \overset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{NMe} \rightarrow \text{CH},$$
 which is converted by alkalis into 5-*oxy-*

1:4-*dimethylpurine 6-methohydroxide*,  

$$\text{OH} \cdot \text{NMe} \cdot \text{CH} \cdot \overset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{NMe} \rightarrow \text{CH};$$

this decomposes and melts at 160°, is stable in the air, and does not absorb carbon dioxide, whilst the solution is strongly alkaline and behaves in every way like that of a strong ammonium base. It is therefore probable that the constitution of the dry salt is represented

by the formula  

$$\text{NMe} \cdot \text{CH} \cdot (\text{OH}) \cdot \overset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{NMe} \rightarrow \text{CH},$$
 and that of the base in

solution by the alternative formula just given. The *chloride*, *bromide*, *picrate*, *platinichloride*, and *aurichloride* have all been prepared. The same base is formed when 5-*oxy-1:4-dimethylpurine methiodide* is converted into the acetate, and the latter decomposed by alkali. From this it follows that the methohydroxide has the constitution assigned to it above, whilst deoxycaffeine is 5-*oxy-1:4:6-trimethyl-*

6:7-*dihydropurine*,  

$$\text{NHMe} \cdot \text{CH}_2 \cdot \overset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{NMe} \rightarrow \text{CH}.$$
 When the methohydroxide is heated at 170–180°, caffeine and deoxycaffeine are formed along with decomposition products of the latter. A. H.

**Constitution of the so-called Oxyazo-compounds.** By R. C. FARMER and ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3089–3101).—The criteria enumerated in this vol., i, 95, are applied to the case in question. Free quinonehydrazone (“hydroxyazobenzene”) is neutral to indicators, is not an electrolyte, and does not form a compound with ammonia in benzene solution; its constitution is probably  $\text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O}$  (and that of its hydrochloride,  $\text{NH}_2\text{PhCl} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O}$ ). But it is a pseudo-acid, for its *sodium* salt, with  $3\text{H}_2\text{O}$ , is only hydrolysed to the extent of about 0.3 per cent. at dilution  $V_{221}$  and therefore must be derived from a comparatively strong acid, probably having the formula  $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{ONa}$ ; moreover, the quinonehydrazone dissolves in aqueous ammonia, probably having undergone a molecular transformation into the hydroxyazo-compound, which then united with ammonia. *p*-Quinonephenylhydrazone forms alkali salts most easily; the *o*-quinonephenylhydrazones (from *o*-toluquinone and from pseudocumquinone) do so less readily and the products are less stable; the meta-isomeride could not be obtained.  $\beta$ -Naphthalene-*o*-quinonephenylhydrazone will only form a salt when treated with the alkoxide; the *p*-chloro- and *p*-nitro-phenylhydrazones form salts with concentrated aqueous potash, but the salts are decomposed by water.

The abnormal hydrates,  $\text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4(\text{OH})_2$  (Hewitt, *Abstr.*, 1895, 353), occupy a position intermediate between the quinonehydrazones and hydroxyazo-compounds; they are best prepared by treating the hydrochlorides of the quinonehydrazones with water or aqueous sodium carbonate or acetate, and they contain 1, or more often  $\frac{1}{2}$ ,  $\text{H}_2\text{O}$ ; a number were prepared, although not all for the first time. Some benzoates and acetates were prepared from the quinone-



hydrazones or their hydrates, and methyl derivatives (azoanisoles,  $\text{NR:N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ ) were prepared from the sodium or silver salts, and also from the nitrosohydrocarbon and the anisidine; in no case was a nitrogen-ether obtained. No hydrazone could be obtained from quinone and phenylhydrazine; quinol, and an oxidation product of phenylhydrazine, diphenyltetrazone, being obtained instead.

The following compounds are, perhaps, new. Derivatives of (*p*-) quinone: *m*-chlorophenylhydrazone, the *methyl* derivative is yellow and melts at  $53^\circ$ ; *o*-tolylhydrazone, the *acetate* melts at  $65^\circ$ , and the *methyl* derivative is brown and melts at  $59^\circ$ ; pseudocumenehydrazone, the *hydrochloride* melts at  $162^\circ$ , and the *methyl* derivative is brown and melts at  $89^\circ$ . Derivatives of *o*-chloroquinone: the *phenylhydrazone* is yellow and melts at  $88^\circ$ , the *hydrochloride* melts at  $150^\circ$ , the *hydrate*, which is brick-red below  $50^\circ$  and yellow above, melts at  $73^\circ$ ; *o*-tolylhydrazone, the *hydrochloride* melts at  $148^\circ$ . Derivatives of *o*-toluquinone: *m*-chlorophenylhydrazone is yellow and melts at  $104^\circ$ , the *hydrate* is red, melts at  $76^\circ$ , does not lose water readily, and is not dissociated in benzene solution, as cryoscopic experiments show, the *benzoate* is pale yellow and melts at  $101^\circ$ ; *o*-tolylhydrazone, the *hydrochloride* melts at  $157^\circ$ , another *hydrate* is brick-red, effloresces readily, and melts at  $83^\circ$ . C. F. B.

**Constitution of the Hydroxyazo-compounds.** By WILLIAM MCPHERSON (*Amer. Chem. J.*, 1899, 22, 364—383).—The early portion of this paper contains details of work already published in brief (Abstr., 1896, i, 27); that the *p*-hydroxyazo-compounds have the constitution denoted by their names, and are not quinone derivatives of the type  $\text{O:R:N:NPh}$ , is held to be established by the following facts. (1) *p*-Hydroxyazobenzene by direct acylation or alkylation, yields derivatives unquestionably of the type  $\text{NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$  ( $\text{R} = \text{acyl or alkyl}$ ), although *o*-hydroxyazo-compounds give by acylation derivatives as unquestionably of the form  $\text{O:R:N:NPhAc}$  (Goldschmidt and others). (2) The free *p*-hydroxyazo-compounds do not interact with phenylhydrazine at  $100^\circ$ , although all *p*-quinone-benzoylphenylhydrazones react explosively with this substance. (3) All *p*-hydroxyazo-compounds are readily soluble in dilute caustic alkalis, whilst the *o*-hydroxyazo-compounds derived from naphthalene, which are undoubtedly quinonephenylhydrazones, are insoluble. (4) The results obtained in the cryoscopic researches of Auwers and Orton (Abstr., 1897, i, 40, and ii, 112).

The hydrazones described were prepared by the interaction of the quinones with salts of the respective hydrazines.

*Quinoneacetylphenylhydrazone*,  $\text{O:C}_6\text{H}_4\cdot\text{N:NPhAc}$ , crystallises from a mixture of benzene and light petroleum in flat, yellow needles, melts at  $118^\circ$ , and is not identical with *p*-acetoxyazobenzene,  $\text{NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$  (Wallach and Kiepenheuer, *Ber.*, 1881, 14, 2617), which melts at  $89.5^\circ$ , not  $84\text{--}85^\circ$ ; when heated with alcoholic potash, however, it yields *p*-hydroxyazobenzene. *Toluquinonebenzoylphenylhydrazone*,  $\text{O:C}_6\text{H}_3\text{Me:N:NPh}\cdot\text{COPh}$ , crystallises from benzene in small, square, yellow plates, and melts at  $151^\circ$ ; when reduced with zinc dust and acetic acid, it yields benzimidide, and is converted by

alcoholic potash into benzeneazo-*o*-cresol, although not identical with the benzoate of the latter (Noelting and Kohn, Abstr., 1884, 901; compare Goldschmidt and Pollak, Abstr., 1892, 974). *Thymoquinonebenzoylphenylhydrazine*,  $\text{O}:\text{C}_6\text{H}_2\text{MePr}^\beta:\text{N}\cdot\text{NPh}\cdot\text{COPh}$ , crystallises from a mixture of benzene and light petroleum in yellow plates and melts at  $132^\circ$ ; there is also formed a colourless, crystalline substance,  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ , melting at  $155^\circ$ . The hydrazine, on reduction with zinc dust and acetic acid, yields benzeneazothymol, but is not identical with the benzoate of the latter,  $\text{OBz}\cdot\text{C}_6\text{H}_2\text{MePr}^\beta:\text{N}_2\text{Ph}$ , prepared by Baumann's reaction, which crystallises from hot alcohol in reddish-yellow needles, melts at  $115^\circ$ , and is converted by alcoholic potash into the parent substance.  *$\alpha$ -Naphthaquinonebenzoylphenylhydrazine* crystallises from a mixture of benzene and light petroleum in yellow, silky needles, and melts at  $161.5^\circ$ ; it is not identical with benzeneazo- $\alpha$ -naphthyl benzoate (Meldola, Trans., 1889, 55, 606).

When benzoquinone and  $\alpha$ -phenylmethylhydrazine hydrochloride are brought together in aqueous solution, nitrogen is evolved and diphenyldimethyltetrazone formed; with toluquinone and thymoquinone, similar action occurs. *Diphenyldibenzyltetrazone*,  $\text{N}_2(\text{NPh}\cdot\text{C}_7\text{H}_7)_2$ , obtained similarly from benzoquinone and  $\alpha$ -phenylbenzylhydrazine sulphate, crystallises from a mixture of benzene and light petroleum in colourless rhombohedra, and melts and decomposes at  $145^\circ$ .  *$\alpha$ -Naphthaquinonephenylmethylhydrazine*,  $\text{O}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NMePh}$ , crystallises in long, flat, amethyst-coloured crystals, melts at  $118.5^\circ$ , and is not identical with 4-benzeneazo- $\alpha$ -naphthol-1-methyl ether,



(Zincke and Bindewald, *Ber.*, 1884, 17, 3026).  *$\alpha$ -Naphthaquinonephenylbenzylhydrazine*,  $\text{O}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NPh}\cdot\text{C}_7\text{H}_7$ , crystallises from a mixture of benzene and light petroleum in yellow, dichroic, flat needles and melts at  $136^\circ$ ; the benzyl ether,  $\text{C}_7\text{H}_7\cdot\text{O}\cdot\text{C}_{10}\text{H}_6:\text{N}_2\text{Ph}$ , prepared by the action of benzyl chloride and caustic soda on benzeneazo- $\alpha$ -naphthol, forms ruby-red monoclinic crystals, and melts at  $102^\circ$ .

The benzoyl derivative,  $\text{O}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NPhBz}$ , is obtained by the action of benzoyl chloride on an alcoholic solution of  $\beta$ -naphthaquinonephenylhydrazine and sodium ethoxide, and also by the interaction of  $\beta$ -naphthaquinone and  $\alpha$ -benzoylphenylhydrazine sulphate; it forms yellow needles, melts at  $191^\circ$ , and on hydrolysis with alcoholic potash or concentrated sulphuric acid, yields benzoic acid and  $\beta$ -naphthaquinonephenylhydrazine. When the latter is heated with methyl iodide and alcoholic sodium methoxide, the methyl ether of 2-benzeneazo- $\alpha$ -naphthol is formed (compare Meldola and Hanes, Trans., 1894, 65, 834; Noelting and Grandmougin, Abstr., 1891, 1076), which crystallises from alcohol in reddish-yellow plates and melts at  $95^\circ$ ;  *$\beta$ -naphthaquinonephenylmethylhydrazine* crystallises from alcohol in yellow needles and melts at  $134.5^\circ$ .

W. A. D.

**Action of Benzoyl Chloride on the Phenylhydrazones of Benzoin.** By PAUL C. FREER (*Amer. Chem. J.*, 1899, 22, 396—402. Compare Smith, Abstr., 1899, i, 909).—The product of the action of benzoyl chloride on benzoin- $\beta$ -phenylhydrazine dissolved in absolute ether at "winter temperature," consists principally of

benzanilide and benzil, together with lophine, dibenzoylaniline, hydrogen chloride, ammonium chloride, and aniline hydrochloride, but a considerable amount of resin is also formed; *m*-nitrobenzoyl chloride, under similar conditions, gives rise to *m*-nitrobenzoylaniline, but the action of benzoyl chloride on benzoin- $\beta$ -phenylhydrazone methyl ether yields only an intractable resin. The author discusses the nature of these reactions at some length, on the assumption that the compound,  $\text{NH} \begin{smallmatrix} \text{CPh} \\ \diagup \quad \diagdown \\ \text{NPh} \end{smallmatrix} \text{CPh}$ , is initially formed; the formation of lophine from benzoin- $\beta$ -phenylhydrazone is explained by assuming that the latter first dissociates into benzaldehyde and the group  $\text{:CPh} \cdot \text{NH} \cdot \text{NHPh}$ , the benzaldehyde subsequently combining with the benzil and ammonia simultaneously formed.

The author reiterates his statement (Abstr., 1899, i, 357) that benzoin- $\alpha$ -phenylhydrazone is not affected by benzoyl chloride.

W. A. D.

**Unsymmetrical Disubstituted Hydrazones.** By HANS LABHARDT and K. VON ZEMBRZUSKI (*Ber.*, 1899, 32, 3060—3063).—The phenylhydrazones of benzaldehyde, salicylaldehyde, and their homologues are white or pale yellow; the hydrazones containing nitro-groups and their sulphonic acids are either yellow or red, the latter compounds dyeing wool and silk from acid baths. The hydrazones derived from secondary hydrazines and aromatic aldehydes have similar properties and the following compounds of this type are described:

*Phenyl-p-nitrobenzylidenemethylhydrazine*,  $\text{NMePh} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , obtained by mixing equivalent amounts of *p*-nitrobenzaldehyde and  $\alpha$ -phenylmethylhydrazine in alcoholic solution, melts at  $132^\circ$ ; the *m-nitro*-compound melts at  $112^\circ$  and the *o-nitro*- at  $77^\circ$ ; these substances form red crystals readily soluble in the ordinary organic solvents; the *para*-compound may also be produced by methylating phenyl-*p*-nitrobenzylidenemethylhydrazine.

*Phenyl-o-hydroxybenzylidenemethylhydrazine* crystallises in white needles and melts at  $71^\circ$ ; its solution in alcoholic potash is yellow.

*Phenyl-p-nitrobenzylidenemethylhydrazine* melts at  $131^\circ$  and the *m-nitro*-compound at  $114^\circ$ ; these substances are red, whilst the *o-nitro*-derivative, which melts at  $44^\circ$ , crystallises in brownish-yellow needles.

*Diphenyl-p-nitrobenzylidenemethylhydrazine* melts at  $131^\circ$ , the *m-nitro*-compound at  $119$ — $120^\circ$ ; both these substances are brownish-yellow; the *o-nitro*-compound melts at  $146^\circ$  and is yellowish-red; the *o-hydroxy*-compound crystallises in white needles and melts at  $139^\circ$ .

*p-Tolyl- $\alpha$ -methylhydrazine*, prepared by reducing *p*-tolylmethylnitrosamine, is a non-crystallisable oil, readily soluble in the ordinary organic solvents; it is decomposed by concentrated mineral acids, its hydrochloride being most conveniently obtained by passing hydrogen chloride into its ethereal solution.

*p-Tolyl-p-nitrobenzylidenemethylhydrazine* melts at  $143^\circ$ , the *m-nitro*-compound at  $150.5^\circ$ , and the *o-nitro* compound at  $90.5^\circ$ ; these nitro-derivatives are red, whilst the *p-hydroxy*-compound melting at  $85$ — $86^\circ$ , is pale yellow.

G. T. M.

**Normal Diazo-compounds as "Pseudodiazonium Compounds."** By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3132—3136).—The relation of normal diazo-compounds (metallic salts, diazo-oxides, diazo-ethers, and normal diazo-cyanides) to diazonium salts exactly corresponds with that of the pseudo-bases (see this vol., i, 113) to the ammonium salts. The non-existence of the isomeric diazonium compounds corresponds with the labile or unstable nature of the ammonium bases, their cyanides and other derivatives, the velocity of change being here too great to be observed.

The latter part of the paper is a reply to Bamberger (*Abstr.*, 1899, i, 750). T. M. L.

**Decomposition of Proteids by Acids.** By THOMAS BOKORNY (*Zeit. angew. Chem.*, 1899, 1099—1100).—The action of 4 per cent. aqueous solutions of hydrochloric, hydrobromic, sulphuric, oxalic, and acetic acids on purified egg-albumin has been studied. The action begins soonest with hydrochloric acid, and the others follow in the order given. The albumoses and peptones formed were separately precipitated after the several mixtures had been boiled for 2 hours. Moderately large quantities of peptone were obtained from the hydrochloric, hydrobromic and sulphuric acid solutions, none at all from the oxalic acid, and merely a trace from the acetic acid. Compare Wroblewski on peptonisation (*Abstr.*, 1895, ii, 516).

J. J. S.

**Amount of Tyrosine from Proteids.** By FELIX REACH (*Virchow's Archiv.*, 1899, 158, 288—296).—The amount of tyrosine obtained from the decomposition of various proteids is very differently given by different observers, and also differs considerably with different proteids (from 0.25 to 5 per cent.).

In the present research, the proteid material was decomposed by pancreatic digestion, but in parallel experiments with the same proteid the results vary. Thus with fibrin, the amount of tyrosine varied from 0.6 to 3.8; with egg-white from 0.1 to 0.6; with muscle proteids, from 1.06 to 1.37 per cent. The one experiment quoted with casein gave a yield of 4.5 per cent. of tyrosine. W. D. H.

**Nomenclature of the Albumins of White of Egg.** By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1899, ii, 480; from *J. Russ. Chem. Soc.*, 1899, 31, 555—556).—The eggs of different birds contain different kinds of albumin, and the author proposes to name the albumin of hen's egg, which is easily crystallised from ammonium sulphate solution, albumin, and the more soluble albumin, albumin (compare *Abstr.*, 1899, i, 655). In other cases, to the albumin which is least soluble in ammonium sulphate solution a name is given which is formed by attaching the termination "in" to the zoological name of the bird, the more soluble albumins being similarly designated by words ending in "inin" and "inidin" in the order of increasing solubility. Thus the amorphous albumin of pigeon's egg is columbin and the more soluble crystalline albumin is columbinin. E. W. W.

**Action of Heat, Dilute Acids, and Alcohol on Albumin.** By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1899, ii, 480—481; from *J. Russ. Chem. Soc.*, 1899, 31, 556—560. Compare Abstr., 1899, i, 655).—When 0.05—0.5 per cent. solutions of albumin in hydrochloric, hydrobromic, phosphoric, pyrophosphoric or metaphosphoric acid are dialysed at the ordinary temperature, acid solutions are obtained in all cases but the last, metaphosphoric acid alone forming a precipitate. The rotatory power of these acid solutions differs from those of the original solutions and is still further increased by heating at 100°. In both cases, compounds of albumin with the acids are formed, and the change of rotatory power must therefore be due to polymerisation or depolymerisation. These polymeric compounds have also a different solubility in water. The compounds obtained by dialysing the cold solutions, when reduced, regenerate the original albumin, but the compounds prepared by heating at 100° yield only amorphous compounds of the same composition. The formula  $\text{Alb}, 5\text{HCl}$ , in which  $\text{Alb} = \text{C}_{255}\text{H}_{422}\text{O}_{83}\text{N}_{63}\text{S}_3$ , is ascribed to the hydrochloride and  $\text{Alb}, 3\text{HBr}$  to the hydrobromide. Phosphoric acid forms compounds containing  $2\text{H}_3\text{PO}_4$ ,  $3\text{H}_3\text{PO}_4$ , and  $4\text{H}_3\text{PO}_4$  respectively, according to the concentration of the acid, and pyrophosphoric acid compounds containing  $3\text{H}_4\text{P}_2\text{O}_7$  or  $7\text{H}_4\text{P}_2\text{O}_7$ . By heating either of the two latter compounds with a 0.2 or a 0.5 per cent. solution of pyrophosphoric acid, the compounds  $\text{Alb}, 4\text{H}_3\text{PO}_4$  or  $\text{Alb}, 5\text{H}_3\text{PO}_4$  are formed respectively. The albumin obtained by evaporating dialysed albumin in a vacuum or by coagulating it at 100° and finally drying at 100° in a stream of hydrogen, has properties which differ from those of the albumin prepared by precipitating with alcohol and ether and drying in a similar manner, although both have the composition given above. E. W. W.

**Solubility of Serum-Globulin in Water.** By EMIL MARCUS (*Zeit. physiol. Chem.*, 1899, 28, 559—575).—Doubt is cast on the hitherto accepted fact that serum-globulin is insoluble in water. It was prepared by several methods from serum and subjected to dialysis; only a small quantity of the globulin was precipitated. The globulin so precipitated and that which remains in solution do not, however, differ in elementary composition, coagulation-temperature, or specific rotatory power. W. D. H.

**Spectroscopy of the Blood.** By V. ARNOLD (*Chem. Centr.*, 1899, ii, 344; from *Centr. med. Wiss.*, 37, 465—468).—The rose-red solution of hæmatoporphyrin in alcohol or chloroform turns violet on adding bromine water. On adding strong hydrochloric acid, the solution becomes steel-blue. When mixed with aqueous caustic potash, a brown colour is obtained; on adding excess of bromine water, the mixture turns a dirty green, and when hydrochloric acid is added in excess a pure green is obtained. Measurements are given of the bands contained in the absorption spectra of these various solutions.

L. DE K.

**Extractives of Muscle.** By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1899, 28, 524—529).—The N:P ratio in various preparations of carniferrin varies considerably according to the method of preparation.

This is due to varying amounts of impurity, of which the principal constituent is an albumose-like substance. W. D. H.

**Nucleons.** By TH. RICHARD KRÜGER (*Zeit. physiol. Chem.*, 1899, 28, 530—534).—By 'salting-out' solutions of muscle nucleon by sodium chloride or magnesium sulphate, the amount of nitrogen is diminished slightly. If ammonium sulphate is used, the phosphorus is lessened also, and the N:P ratio sinks. These results show that decomposition occurs. A corresponding effect is produced by peptic and tryptic digestion. Similar experiments with milk nucleon gave the same results, except that peptic digestion produces no change and ammonium sulphate causes little or no precipitation.

W. D. H.

**Plasmic Acid.** By ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1899, 28, 426—438).—This substance was originally prepared from yeast nuclein by Kossel (*Abstr.*, 1893, i, 680), and differs in many of its characters from nucleic acid. It is now shown to be metaphosphoric acid. As prepared, however, it contains about 1 per cent. of iron, although whether this is to be regarded as 'organic' or 'masked' iron is uncertain, the various colour reactions giving contradictory results.

W. D. H.

**Properties of Gelatin.** By CARL THORE MÖRNER (*Zeit. physiol. Chem.*, 1899, 28, 471—523).—By treating gelatin in succession with water, dilute potash, dilute acetic acid, water, alcohol, and warm water, filtering, precipitating with alcohol, drying, powdering, extracting with ether, &c., a product was obtained containing only from 0.25 to 0.75 per cent. of ash. It contains 0.2 per cent. of sulphur; this is present in the gelatin, not in impurities; the higher percentage of sulphur given by others is due to proteid admixture. With Millon's reagent, it gives a reaction which, however, is transitory unless the reagent is considerably diluted with water. With sodium chloride, potassium ferrocyanide, and acetic acid, it gives a precipitate when these reagents are present in suitable proportions. The idea that gelatinisation depends on the presence of mineral constituents was not confirmed; neither was any support found for what Dastre calls the 'salt-digestion' of gelatin.

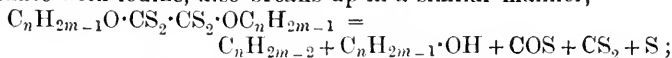
W. D. H.

**Cystin, a Decomposition Product of Keratin.** By KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1899, 28, 595—615).—Horn was treated on the water-bath with 25 per cent. hydrochloric acid for several days; among the products of decomposition (tyrosine, &c.) separated out, most interest attaches to the presence of cystin, 11 grams of which were obtained from 450 grams of dry keratin; cystein was also obtained. In another experiment, more cystin was obtained in proportion, but no cystein.

W. D. H.

## Organic Chemistry.

**New Method of Preparing Unsaturated Hydrocarbons.** By L. TSCHUGAEFF (*Ber.*, 1899, 32, 3332—3335).—When an alkyl xanthate of the unsaturated hydrocarbon radicle  $C_nH_{2m-1}$  is subjected to dry distillation, it breaks up in accordance with the following equations,  $C_nH_{2m-1}O \cdot CS \cdot SR = C_nH_{2m-2} + COS + RSH$  and  $C_nH_{2m-1}O \cdot CS \cdot SR = C_nH_{2m-2} + CS_2 + ROH$ . In both reactions the unsaturated hydrocarbon is obtained, and the yield is usually very good. The dioxanthate, produced by the condensation of a metallic xanthate with iodine, also breaks up in a similar manner,



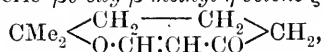
the yield in this case, however, is smaller and the product less pure. These two synthetical methods have been successively employed for the preparation of menthene. Menthol, dissolved in dry toluene, is successively treated with sodium, carbon disulphide, and methyl iodide; the xanthate thus produced, on distillation, yields menthene and methyl mercaptan. The hydrocarbon is purified by fractionation and distillation over sodium; its specific gravity and boiling point correspond with those of other preparations, but its specific rotatory power is far greater; in menthene from the xanthate,  $[\alpha]_D$  varies from  $114.77^\circ$  to  $116.06^\circ$ , whilst in the specimen from the dioxanthate it is  $111.56^\circ$ . The nitrosyl chloride of the most active menthene melts at  $127^\circ$  and gives  $[\alpha]_D$   $242.5^\circ$ . The menthene prepared by Urban and Kremers has a specific rotation of  $32.77^\circ$ ; its nitrosyl chloride melts at  $128^\circ$  and has  $[\alpha]_D$   $13.76^\circ$  (compare *Abstr.*, 1894, i, 468).

G. T. M.

**Biochemical Oxidation of Propylene Glycol.** By ANDRÉ KLING (*Compt. rend.*, 1899, 129, 1252—1254. Compare *Abstr.*, 1899, i, 323).—The aldehydic substance produced by the action of the sorbose bacterium on solutions of propylene glycol is shown to be acetol by isolating it in the form of its oxime. The amount of the glycol oxidised never exceeds 50 per cent. of the total quantity, however long the fermentation is continued; this may be due either to the paralysing effect of the acetol on the bacterium, or to the organism's preference for one of the optical forms of the glycol, or to a combination of the two causes. The unaltered propylene glycol is optically active and appears to consist of a mixture of the dextrorotatory form and the racemic compound. Le Bel, who also effected a partial resolution of propylene glycol by the action of various ferments and moulds, found that the solutions generally became levorotatory. G. T. M.

**Cyclic Isomeric Change of Methyloctadienonol.** By GEORGES LÉSER (*Bull. Soc. Chim.*, 1899, [iii], 21, 969—973. Compare *Abstr.*, 1899, i, 743).—Methyloctadienonol, the product of the condensation of methylheptenone with ethyl formate, has the constitution  $CMO_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH \cdot CH \cdot OH$ , as is shown by its behaviour

towards methylaniline (Abstr., 1899, i, 415) and by its yielding a *monoacetate*, a colourless, odourless liquid boiling at  $138^{\circ}$  under 13 mm. pressure. When heated for a few minutes at  $100^{\circ}$  with five times its weight of 80 per cent. sulphuric acid, methyloctadienonol is converted into the isomeric  $\beta\theta$  *oxy- $\beta$ -methyl- $\eta$ -octene- $\zeta$ -one*,



which melts at about  $-2.5^{\circ}$  and boils without decomposition at  $225\text{--}227^{\circ}$ ; it is insoluble in cold alkalis, gives no coloration with ferric chloride, and is not acted on by chromic acid mixture, but immediately decolorises bromine or potassium permanganate solution. It forms an *oxime* melting at  $90\text{--}91^{\circ}$  and boiling at  $150\text{--}151^{\circ}$  under 18 mm. pressure, which yields an *acetyl* derivative boiling at  $158\text{--}160^{\circ}$  under 20 mm. pressure; oxidation with 2 per cent. potassium permanganate solution converts it into the lactone of  $\gamma$ -hydroxy-isohexoxic acid. The constitution which has been assigned above to the isomeride of methyloctadienonol is fully confirmed by these reactions, and also by a determination of its molecular refraction (found, 44.02; calculated, 43.95). N. L.

**Methylene Sulphate or Sulphuric Methylal.** By MARCEL DELÉPINE (*Compt. rend.*, 1899, 129, 831—833).—Methylene sulphate

or sulphuric methylal,  $\text{CH}_2 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{SO}_2$  or  $\text{CH}_2\text{O}, \text{SO}_3$ , obtained by dissolving trioxymethylene in fuming sulphuric acid, is a white, crystalline, odourless, and tasteless substance, almost insoluble in water and organic solvents with the exception of acetone, from which it can be crystallised and from which it is precipitated by adding water, alcohol, ether, or chloroform. It melts at about  $155^{\circ}$ , but even below this temperature decomposes into sulphur dioxide, carbonic oxide, sulphuric acid, and formaldehyde; in sealed tubes at  $200^{\circ}$ , it yields the same products together with carbon dioxide and a black, solid  $\text{nC}_5\text{H}_6\text{O}$ . Methylene sulphate immediately converts aldehyde into paraldehyde; it is but slightly affected by water or alkalis at the ordinary temperature, but at  $60\text{--}70^{\circ}$  is rapidly hydrolysed, yielding formaldehyde and sulphuric acid. Although it has no action on alcohols in the cold, it reacts at  $60\text{--}70^{\circ}$  with methyl, ethyl, propyl, isopropyl, isobutyl, isoamyl, and benzyl alcohols, yielding the corresponding formals and acid sulphates of the various radicles.

The heat of combustion of methylene sulphate (1 gram) is 1286.5 cal.; molecular heat of combustion at constant pressure and volume, 141.5 Cal. Hence  $\text{S}(\text{oct.}) + \text{O}_4 + \text{C} + \text{H}_2 = \text{SO}_4\text{CH}_2$  solid, develops +162.9 Cals., and the formation of the compound from sulphur trioxide and trioxymethylene develops +18.7 Cals. This reaction is also exothermic if sulphuric acid is substituted for the oxide, owing to the heat of combination of the excess of acid with the water that is formed. C. H. B.

**Velocity and Limits of the Esterification of Phosphoric Acid by Glycerol.** By HENRI IMBERT and GUILLAME BELUGOU (*Bull. Soc. Chim.*, 1899, [iii], 21, 935—939. Compare Abstr., 1899, i, 659.—When phosphoric acid and anhydrous glycerol are mixed in molecular



proportion, monoglycerophosphoric acid alone is formed, the coefficient of esterification reaching its maximum value almost immediately at the ordinary temperature, and then slowly diminishing. At a higher temperature ( $105^{\circ}$ ), the diminution is more rapid, a minimum value being soon reached, after which the coefficient of esterification increases, and ultimately exceeds its original value. The presence of water greatly diminishes the rate of esterification, only 9.32 per cent. of the monohydrated acid being transformed after 13 days at  $50^{\circ}$ . The action of glycerol on phosphoric oxide results in the formation of each of the three glycerophosphoric acids. N. L.

**Acid Esters of Boric Acid.** By ALFRED WOHL and C. NEUBERG (*Ber.*, 1899, 32, 3488—3492).—Hydroxychloropropionacetal,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}(\text{OEt})_2$ , is obtained by treating acetaldehydeacetal with bleaching powder and boric acid in aqueous solution (*Abstr.*, 1898, i, 556); when an attempt is made to prepare glyceraldehydeacetal by boiling the resulting solution with potassium carbonate, ether extracts from the product a *potassium* salt of the composition  $\text{OK}\cdot\text{B}[\text{O}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}(\text{OEt})_2]_2$ .

By treating allyl alcohol with calcium hypobromite and boric acid,  $\beta$ -bromohydrin, melting at  $227\text{--}230^{\circ}$ , was obtained in very small yield; by boiling it with aqueous potassium carbonate and boric acid, and extracting the product with ether, a *potassium* salt,  $\text{OK}\cdot\text{B}[\text{O}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})_2]_2$ , was obtained.

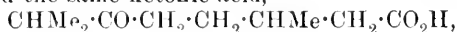
$\beta$ -Bromohydrin  $\alpha$ -ethyl ether appears to react in a similar way; it is made by acting on sodium allyl oxide with ethyl bromide, and treating the product with hypobromous acid. Compounds which do not contain a secondary halogen atom, such as ethyl bromide, benzyl chloride, or the chlorohydrin  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , do not form salts of the kind described, neither do simple secondary halogen derivatives, such as isopropyl chloride and bromide. C. F. B.

**$\alpha$ -Dimethylisocrotonic (2-Dimethyl-3-butinoic) Acid.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1062—1065).—The action of acetaldehyde on ethyl bromoisobutyrate in the presence of zinc, according to Saytzeff and Reformatsky's process, results principally in the formation of *ethyl  $\beta$ -hydroxy- $\alpha$ -dimethylbutyrate*, but symmetrical *diethyl pentamethylbutarate*,  $\text{CHMe}(\text{CMe}_2\cdot\text{CO}_2\text{Et})_2$ , is also produced. The latter boils at  $170\text{--}180^{\circ}$  under 18 mm. pressure, and has a sp. gr. 0.9953 at  $0^{\circ}$ . Ethyl  $\beta$ -hydroxy- $\alpha$ -dimethylbutyrate is a colourless liquid which boils at  $93\text{--}94^{\circ}$  under 18 mm. pressure and has a sp. gr. 0.9974 at  $0^{\circ}$ ; it is not affected by most dehydrating agents, but when heated at  $100^{\circ}$  with phosphorus pentachloride yields *ethyl  $\beta$ -chloro- $\alpha$ -dimethylbutyrate*, which boils at about  $200^{\circ}$  and is not decomposed by alcoholic potash, and *ethyl  $\alpha$ -dimethylisocrotonate*, a colourless liquid boiling at  $144\text{--}146^{\circ}$ , which differs from the alkyl salts of  $\alpha\beta$ -unsaturated acids in not reacting with ethyl sodiomalonate.  *$\alpha$ -Dimethylisocrotonic acid*, obtained by hydrolysing its ethyl salt, is a colourless liquid which boils at  $92^{\circ}$  under 23 mm. pressure and readily combines with bromine to form a crystalline additive product melting at  $91^{\circ}$ . The chloride of this acid reacts with tetrachloroquinol to form two compounds, of the composition  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{C}_6\text{H}_3\cdot\text{Cl}_3$  and

$C_6Cl_4(CO_2 \cdot C_5H_9)_2$  respectively; the former crystallises in white needles, melts at  $132^\circ$ , and is very soluble in neutral solvents, whilst the latter melts at  $133\text{--}134^\circ$  and is only slightly soluble in neutral solvents. N. L. 4

**Ethyl Acetoacetate.** By HEINRICH GOLDSCHMIDT and LAZAR OSLAN (*Ber.*, 1899, 32, 3390—3399).—The hydrolysis of ethyl acetoacetate by sodium hydroxide proceeds as a reaction of the first, and not of the second, order, the velocity constant being independent of the concentration of the ester and of the base. This result can be explained if (1) ethyl acetoacetate is a strong monobasic acid and is converted almost completely into the sodium derivative by an equivalent of sodium hydroxide, whilst (2) sodium acetoacetate possesses no marked acid properties, and (3) if the hydrolysis takes place by the action of the free alkali on the free ester and not on its sodium derivative. The last statement is supported by Fischer's observation that metallic compounds of esters are hydrolysed only with difficulty (*Abstr.*, 1899, i, 262), and especially that ethyl acetoacetate is hydrolysed more slowly than ethyl dimethylacetoacetate, which does not form a metallic derivative. The neutral character of sodium acetoacetate is shown by the fact that it does not produce any marked decrease in the velocity of hydrolysis of ethyl acetate by sodium hydroxide. The acid character of ethyl acetoacetate is shown by conductivity determinations which gave  $\mu_{16}$  0.36 and  $\mu_{1024}$  3.12,  $\mu_\infty$  360,  $\kappa$   $0.63 \times 10^{-7}$  at  $25^\circ$ ; the ester is thus a much stronger acid than phenol, and slightly stronger than *o*-cresol. The hydrolytic constant of ethyl sodioacetoacetate is calculated to be  $\kappa = 2 \times 10^{-7}$  and the small extent of the dissociation is confirmed by cryoscopic measurements. T. M. L.

**Orientation in the Terpene Series. XXIV.** By ADOLF VON BAEYER (*Ber.*, 1899, 32, 3619—3624) [with OTTO SEUFFERT].—Although  $\beta\zeta$ -dimethyloctane- $\epsilon$ -oleic acid contains its hydroxyl group in the  $\epsilon$ -position relatively to the carboxyl group, it behaves like a  $\gamma$ - or  $\delta$ -hydroxy-acid and yields a lactone,  $\beta\zeta$ -dimethyloctane- $\epsilon$ -olide,  $CHMe-CH_2-CO-CH_2 \cdot CH_2 \cdot CHPr^s > O$ , produced when the corresponding hydroxy-acid (*Abstr.*, 1896, i, 217) is heated in a vacuum, distils at  $128\text{--}130^\circ$  under 17 mm. pressure; when cooled in a freezing mixture, it becomes solid, and as the temperature of the mass rises one portion melts, whilst the residue remains solid in the form of tabular crystals which melt at  $47^\circ$ . Analysis indicates that the two fractions are isomeric; both modifications are insoluble in water and cold dilute caustic soda solution; they dissolve in the hot alkali, but are not attacked by potassium permanganate. The lactone melting at  $47^\circ$  yields an acid melting at  $65^\circ$ , whilst that of lower melting point yields an oily acid. The isomerism of the lactones and their acids depends on the presence of two asymmetric carbon atoms in the molecule of the hydroxy-acid,  $CHMe_2 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CO_2H$ ; one of these is suppressed by oxidation, and accordingly both modifications of this compound yield the same ketonic acid,

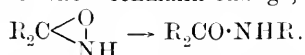


on treatment with potassium dichromate and sulphuric acid; the ketone is identified by means of the oxime which melts at 97°.

G. T. M.

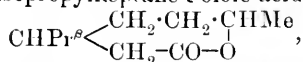
**Action of Caro's Reagent on Ketones.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1899, 32, 3625—3633. Compare Caro, *Zeit. angew. Chem.*, 1898, 845).—When Caro's reagent (potassium persulphate and sulphuric acid) acts on a ketone, an oxygen atom is introduced into the molecule between the carboxyl group and one of the hydrocarbon residues; if it is assumed that the first product is a

peroxide, then the course of the reaction  $R_2C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} \rightarrow R \cdot CO \cdot OR$  is comparable with that of the Beckmann change,



When menthone is treated with a mixture of persulphate and concentrated sulphuric acid, the  $\epsilon$ -lactone of  $\beta\zeta$ -dimethyloctane- $\epsilon$ -olonic acid is produced (compare preceding abstract).

The  $\epsilon$ -lactone of  $\beta$ -isopropylheptane- $\epsilon$ -olonic acid,



prepared from tetrahydrocarvone in a similar manner, is an oil boiling at 155—156° under 21 mm. pressure. On hydrolysis, the lactone yields an uncrystallisable hydroxy-acid, the silver salt of which crystallises in white needles; this acid, when treated with Beckmann's mixture, yields a ketonic acid identical with that obtained by direct oxidation from tetrahydrocarvone (*Abstr.*, 1896, i, 217).

Campholide is produced when a benzene solution of camphor is added to a mixture of potassium persulphate, sulphuric acid, and water ( $H_2SO_4 \cdot H_2O$ ), and is isolated by means of its additive compound with hydrogen bromide. The latter compound, *bromocampholic acid*, crystallises in plates and melts at 177°. The campholide is identical with that obtained by Haller from camphoric anhydride. The compound  $C_{10}H_{16}O_4$  is obtained as a bye-product in the above reaction; it crystallises from water in plates and melts at 189—190°.

A compound having the composition of acetone peroxide is obtained from acetone and persulphuric acid; it crystallises in prisms, melts at 132—133°, and closely resembles the acetone peroxide obtained by Wolfenstein from acetone and hydrogen peroxide; the latter, however, melts at 94—95° (*Abstr.*, 1895, i, 644).

Terpineol, when treated with Caro's reagent, yields trihydroxy-hexahydrocymene.

G. T. M.

**Action of Aluminium Chloride on Camphoric Anhydride.** By G. BLANC (*Compt. rend.*, 1899, 129, 1019—1020. Compare Lees and Perkin, *Proc.*, 1898, 14, 111; 1899, 15, 23; 1900, 16, 18).—When the bye-product obtained in the preparation of isolauronic acid by the action of aluminium chloride on camphoric anhydride is distilled in a vacuum, the distillate consists of unchanged camphoric anhydride, isolauronic acid, and an oily liquid boiling at 140—145° under 20 mm. pressure. This oily liquid, by repeated extraction with potassium hydrogen carbonate, is separated into an acid portion (A) and a neutral portion (B).

The acid portion (*A*) boils at 140—142° under 20 mm. pressure, and consists of a mixture of several acids of the composition  $C_9H_{14}O_2$  and  $C_9H_{16}O_2$ . It was oxidised with alkaline potassium permanganate and the oxidation product distilled in steam. The residue in the flask consists of the products of oxidation of isolauroic and isolaurolic acids, and an oily, non-ketonic acid which is unsaturated and probably has the composition  $C_9H_{14}O_2$ . The distillate consists of two saturated acids,  $C_9H_{16}O_2$ ; the first melts at 76—77° and forms an amide crystallising in needles and melting at 190°, and a bromoethyl ester, boiling at 130—132° under 25 mm. pressure, which, when treated with alcoholic potash, gives an acid,  $C_9H_{14}O_2$ , melting at 108—110°, the amide of which melts at 163°. The second acid found in the distillate is an uncrystallisable oil of high boiling point possessing a fatty acid odour; its amide is a liquid.

The neutral portion (*B*) is probably the lactone of an acid,  $C_9H_{16}O_3$ ; it boils at 125—135° under 30 mm. pressure, is insoluble in cold dilute alkalis, but dissolves on warming, and on analysis gives numbers corresponding with the formula  $C_9H_{14}O_2$ .  
H. R. LE S.

**Camphenilanaldehyde and Camphenilanic Acid.** By JULIUS BREDT and WILHELM JAGELKI (*Annalen*, 1899, 310, 112—134. Compare Abstr., 1898, i, 264).—It has been shown by Étard (Abstr., 1893, i, 360) that camphene forms the additive compound  $C_{10}H_{16} \cdot 2CrO_2Cl_2$  when dissolved in carbon disulphide and treated with chromyl dichloride; treatment with water gives rise to an aldehyde, to which he ascribed the formula  $C_{10}H_{14}O$ , calling it camphenaldehyde, and this, on exposure to air, yields the corresponding acid, which was called camphenic acid. The authors, however, find that the aldehyde has the formula  $C_{10}H_{16}O$ , and they use the name camphenilanaldehyde; the acid  $C_{10}H_{16}O_2$  is now called camphenilanic acid.

The double compound,  $C_{10}H_{16} \cdot 2CrO_2Cl_2$ , is a pale brown powder which is very hygroscopic, forming a green liquid when exposed to air; it tastes sweet, and is somewhat soluble in ether, being insoluble in benzene, petroleum, or carbon tetrachloride.

Camphenilanaldehyde,  $\begin{array}{c} CH_2 \cdot CH \\ | \quad \quad \quad \diagup \\ CH_2 \cdot CMe \end{array} > CMe_2$   $\rightarrow$   $CH \cdot CHO$ , produced by the

action of water on the double compound of camphene with chromyl dichloride, has an agreeable odour, and dissolves readily in organic solvents; it melts at about 70°, and boils at 96° under 14 mm. pressure.

Camphenilanic acid,  $\begin{array}{c} CH_2 \cdot CH \\ | \quad \quad \quad \diagup \\ CH_2 \cdot CMe \end{array} > CMe_2$   $\rightarrow$   $CH \cdot CO_2H$ , melts at 65° and

boils at 147° under 14 mm. pressure; the calcium and silver salts are crystalline and anhydrous. The chloride,  $C_{10}H_{15}OCl$ , boils at 105—106° under 14 mm. pressure, and the methyl ester boils at 99—100° under 12 mm. pressure.

Bromocamphenilanic acid,  $C_{10}H_{15}O_2Br$ , separates from petroleum in colourless crystals and melts at 145°; the chloride, prepared by the action of bromine on camphenilanic chloride, is a white, crystalline substance, and boils at 165° under 14 mm. pressure.

Isocamphenilanic acid,  $C_{10}H_{16}O_2$ , prepared by heating camphenilanic

acid with dilute nitric acid, melts at  $118^{\circ}$ , and separates from petroleum in crystals belonging to the triclinic system; [ $a:b:c = 1.8852:1:1.2155$ ;  $\alpha = 69^{\circ}3'30''$ ,  $\beta = 99^{\circ}20'$ ,  $\gamma = 99^{\circ}0'30''$ ]. It is also produced on oxidising camphenilanaldehyde with potassium permanganate; the calcium salt contains  $2H_2O$ , and the silver salt resists the action of light.

*Hydroxycamphenilanic (campheniloloic) acid*,  $C_{10}H_{16}O_3$ , prepared by heating bromocamphenilanic acid with sodium carbonate, melts at  $170-172^{\circ}$ ; the sodium salt is not readily soluble in cold water, and the silver salt is crystalline.

It is probable that camphenilanaldehyde is identical with the aldehydic substance obtained by Wagner from camphene glycol and hydrochloric acid, and hydroxycamphenilanic acid is most likely identical with the acid obtained by Wagner on oxidising camphene with potassium permanganate (compare also Jagelki, Abstr., 1899, i, 627).  
M. O. F.

**Preparation of Azelaic Acid.** By LÉON MAQUENNE (*Bull. Soc. Chim.*, 1899, [iii], 21, 1061—1062).—Azelaic acid is usually obtained by oxidising castor oil with nitric acid, but a purer product and a larger yield are more readily obtained by the action of potassium permanganate on an alkaline solution of the crude ricinoleic acid obtained by the hydrolysis of the oil.  
N. L.

**Malic Acid from Hippophæ Rhamnoides.** By HUGO ERDMANN (*Ber.*, 1899, 32, 3351—3354. Compare this vol., i, 10).—The malic acid obtained from the ripe berries of *Hippophæ rhamnoides* (Seabuckthorn) is identical with that isolated from mountain ash berries; their ammonium salts have the same molecular rotation ( $2.89-2.94^{\circ}$ )

Calcium malate separates from hot aqueous solutions in crystals containing  $1\frac{1}{2}H_2O$ . The berries also contain other acidic substances and mannitol, the latter being isolated in the form of its calcium derivative.  
G. T. M.

**Some Complex Salts of Tartaric and Malic Acids, and their Specific Rotatory Power.** By ARTHUR ROSENHEIM and HERRMANN ITZIG (*Ber.*, 1899, 32, 3424—3440).—The potassium, sodium, and ammonium “diberylliumtartrates,”  $M'_2O, 4BeO, 2C_4H_4O_5$ , previously described (Abstr., 1898, ii, 71) have been examined as regards their optical activity; the specimens prepared contained respectively 6, 9, and  $9H_2O$ . The molecular rotation,  $[M]_D$ , at  $20^{\circ}$  in aqueous solution, is about  $225^{\circ}$ ,  $225^{\circ}$ , and  $242^{\circ}$  respectively, and varies but little with the dilution; it is due to a complex anion,  $(C_8H_4O_{13}Be_4)^-$  or  $(C_4H_3O_7Be_2)^-$ , of the nature  $(-CO_2 \cdot [C_2H_3O_2Be] \cdot CO_2 \cdot Be)_2O$  or  $-CO_2 \cdot [C_2H_3O_2Be] \cdot CO_2 \cdot Be \cdot OH$ ,

and exceedingly stable, since dilution does not affect the rotation and so cannot produce hydrolysis. Potassium and ammonium “monoberylliumtartrates,”  $M'_2O, 2BeO, 2C_4H_4O_5 + 2H_2O$  (*loc. cit.*, 72), were examined in the same way (the sodium salt, with  $3H_2O$ , could not be obtained sufficiently pure); the molecular rotation at  $20^{\circ}$  was about  $125^{\circ}$  and  $126^{\circ}$  respectively, and varied but little with the dilution; it was probably due to a stable complex anion,  $(C_5H_3O_{13}Be_2)^-$ , of the nature  $(-CO_2 \cdot [CH \cdot OH]_2 \cdot CO_2 \cdot Be)_2O$ . By dissolving an equivalent

amount of beryllium hydroxide in a boiling solution of tartaric acid, a *beryllium tartrate*,  $C_4H_2O_7Be_3 + 7H_2O$ , was obtained; this has, at  $20^\circ$ , a molecular rotation of about  $171^\circ$  in 3 per cent. solution, increasing with the dilution. In all cases, the entrance of beryllium into the molecule causes a great increase in the rotatory power. *Ammonium di- and mono-beryllium racemates* were also prepared; they have the same composition as the *d*-tartrates; but they are optically inactive, so that the *l*-tartrate molecule must have been affected in the same degree as the *d*-molecule, and in the opposite sense, by the entrance of the beryllium.

Similar observations were made in the case of malic acid. *Potassium, sodium, and ammonium diberylliummalates*,  $M'_2O, 4BeO, (C_4H_3O_3)_2O$ , with 5, 7, and  $4H_2O$  respectively, were prepared by saturating boiling aqueous solutions of the alkali-hydrogen malate with freshly precipitated beryllium hydroxide. The molecular rotation is about  $-199^\circ$  at  $16^\circ$ ,  $-202^\circ$  at  $16^\circ$ , and  $-201^\circ$  at  $13^\circ$  respectively, and is due to an anion of the nature  $-CO_2 \cdot CH_2 \cdot CH \begin{smallmatrix} \text{O} \cdot Be - O - Be \cdot O \\ \text{CO}_2 \cdot Be \cdot O \cdot Be \cdot CO_2 \end{smallmatrix} > CH \cdot CH_2 \cdot CO_2^-$ .

*Ammonium monoberylliummalate*,  $(NH_4)_2O, 2BeO, 2C_4H_4O_4 + H_2O$ , prepared like the analogous tartrate, has a molecular rotation of about  $-106^\circ$  at  $20^\circ$ .

By adding beryllium sulphate and sodium hydroxide in varying proportions to solutions of tartaric or malic acids, the molecular rotation reached a maximum when the proportions corresponded with the formation of the "diberyllium" salt, and was then about equal to that of the pure salt. Ethyl hydrogen tartrate gave a maximum rotation when the proportions were  $C_6H_{10}O_6, 2BeSO_4, 4KOH$ . The rotatory power of quinic and *d*-chlorosuccinic acids, which contain no alcoholic hydroxyl groups, is not affected by the addition of beryllium sulphate (and alkali); nor is that of dextrose.

Neither magnesium, zinc, nor cadmium forms complex tartrates or malates like those formed by beryllium, nor do their salts affect the rotatory power of alkaline tartrates or malates. C. F. B.

**Action of Nitric Acid on Acids of the Fatty Series which contain the Isopropyl Group.** By JULIUS BREDT and J. B. C. KERSHAW (*Ber.*, 1899, 32, 3661—3666. Compare Abstr., 1883, 176).—The experiments of the authors have been extended to dibasic acids which have been found to behave in a similar manner to the monobasic acids which had been previously examined.

Terebic acid is converted by the continued action of nitric acid into  $\gamma$ -valerolactone- $\beta\gamma$ -dicarboxylic acid,  $CH_2 \begin{smallmatrix} \text{CH}(\text{CO}_2\text{H}) \\ \text{CO} \text{---} \text{O} \end{smallmatrix} > CMe \cdot \text{CO}_2\text{H}$ , which has already been prepared by Rach (Abstr., 1886, 1012). The *diethyl* ester boils at  $174$ — $175^\circ$  under 9 mm. pressure. Isopropylsuccinic acid (pimelic acid) is also converted by nitric acid into valerolactonedicarboxylic acid. These two compounds therefore behave in a precisely similar manner to isohexanoic acid and isohexolactone. A. H.

**Natural Cyclic Isomeric Change of Citronellal.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1023—1025. Compare Abstr., 1899, i, 622).—Pure citronellal is very unstable, and spon

taneously undergoes the same isomeric change which is effected more rapidly by the action of acids. A specimen which had been kept for two months was found to be almost entirely converted into isopulegol, which was identified by oxidising it with chromic acid mixture, and converting the isopulegone thus formed into the mixture of two isomeric semicarbazones which is characteristic of this substance. In the presence of hydrocarbons and terpenylic alcohols, such as occur in commercial specimens, citronellal is much more stable.

N. L.

**Formation of Barium Citryl and Citronellyl Sulphites.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1026—1027).—In reply to the remarks of Tiemann (*Abstr.*, 1899, i, 622), the author states that it is not contended that an accurate quantitative separation of citral from citronellal can be effected by the process described by Flatau and Labbé (*loc. cit.*). The barium hydrogen sulphite compound of citronellal is precipitated immediately to the extent of about 85 per cent. of the theoretical amount, whilst the yield of the corresponding citral derivative never exceeds 27—28 per cent., and in the first five minutes only amounts to 17—18 per cent. The citral compound, moreover, is contaminated with barium sulphite, whereas the citronellal derivative is precipitated in a pure state.

N. L.

**Derivatives of the Isuretine of Formhydroxamic Acid and their Relation to Fulminic Acid.** By H. C. BIDDLE (*Annalen*, 1899, 310, 1—24. Compare Nef, *Abstr.*, 1896, i, 71).—*Ethylisuretine*,  $\text{NH}_2\cdot\text{CH}\cdot\text{NOEt}$ , has been described already as ethoxyformamidine (Nef, *Abstr.*, 1895, i, 12).

*Benzylisuretine*,  $\text{NH}_2\cdot\text{CH}\cdot\text{NO}\cdot\text{CH}_2\text{Ph}$ , prepared from isuretine by the action of benzyl chloride and alcoholic potash, crystallises from petroleum in slender needles and melts at  $58^\circ$ ; hot concentrated hydrochloric acid eliminates  $\alpha$ -benzylhydroxylamine, and nitrous acid gives rise to a variety of products, including benzaldehyde, benzyl alcohol, and benzylchloro-formoxime. The *platinichloride* crystallises in yellow, rhombic plates and melts at  $157$ — $158^\circ$ .

*Methylisuretine*,  $\text{NH}_2\cdot\text{CH}\cdot\text{NOMe}$ , crystallises from light petroleum in plates and melts at  $40$ — $40.5^\circ$ .

An attempt to prepare the benzyl derivative of fulminic acid by the action of chloroform and alcoholic potash on  $\alpha$ -benzylhydroxylamine gave rise to the compound  $\text{C}_8\text{H}_9\text{O}_2\text{N}$ , which crystallises from petroleum in colourless leaflets and melts at  $86$ — $86.5^\circ$ ; a mixture of benzyl alcohol and benzyl ether is also produced, along with a substance having the odour of an isonitrile.

*Benzylformhydroxamic acid*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NH}\cdot\text{CHO}$ , obtained by heating  $\alpha$ -benzylhydroxylamine with formic acid, is a viscous, colourless oil, which boils at  $170^\circ$  under 15 mm. pressure, when it decomposes slightly; cold, concentrated hydrochloric acid resolves it into formic acid and  $\alpha$ -benzylhydroxylamine hydrochloride. The *silver* derivative is amorphous, and yields benzaldehyde when heated.

*Benzylchloro-formoxime*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CHCl}$ , produced by the action of phosphorus pentachloride on benzylformhydroxamic acid, is a

colourless liquid having an odour of fir-wood; it boils at  $101^{\circ}$  under 11 mm. pressure, and at  $210^{\circ}$  under atmospheric pressure. It is a stable substance, and is devoid of basic properties; hydrochloric acid eliminates  $\alpha$ -benzylhydroxylamine quantitatively.

Formhydroxamic acid has been investigated by Jones (Abstr., 1898, i, 173). It displays a great tendency to dissociate into hydroxylamine and carbon monoxide, decomposing in this way when heated a few degrees above the melting point. The solution in acetone undergoes spontaneous change in the course of a few days, yielding acetoxime. The sodium salt decomposes into ammonia and sodium carbonate. The lead salt separates from water in colourless, transparent crystals containing water, and explodes at  $145^{\circ}$ ; when dried at  $100^{\circ}$ , it yields ammonia and lead carbonate.

*Chloro-formoxime benzoate*,  $\text{COPh}\cdot\text{O}\cdot\text{N}:\text{CHCl}$ , obtained from the benzoate of formhydroxamic acid by the action of phosphorus pentachloride, crystallises from ether in odourless needles and melts at  $53\cdot5$ — $54\cdot5^{\circ}$ ; aniline converts it into benzanilide and chloro-formoxime, the latter yielding phenylisouretine.

*Chloro-formoxime acetate*,  $\text{COMe}\cdot\text{O}\cdot\text{N}:\text{CHCl}$ , prepared from the acetate of formhydroxamic acid and phosphorus pentachloride, boils at  $60$ — $63^{\circ}$  under 15 mm. pressure; it has a penetrating odour resembling that of chloro-formoxime, and gives rise to similar physiological effects. When the purified substance is heated with a concentrated aqueous solution of silver nitrate, it is decomposed slowly, yielding silver fulminate, silver chloride, and acetic acid.

*Ethyl  $\alpha$ -benzyloximiniformic ether*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}:\text{CH}\cdot\text{OEt}$ , is the more volatile of the two isomerides produced by the action of ethyl iodide on the silver salt of benzylformhydroxamic acid, and boils at  $121$ — $122^{\circ}$  under 15 mm. pressure, having the refractive index  $n_D$   $1\cdot5105$ ; alcoholic hydrochloric acid gives rise to  $\alpha$ -benzylhydroxylamine, whilst the gas eliminates ethylic chloride. The  $\beta$ -modification boils at  $149$ — $150^{\circ}$  under 15 mm. pressure, and has  $n_D$   $1\cdot5256$ ; in chemical behaviour, it resembles the isomeride.

*$\alpha$ -Benzyloximiniformyl acetyl oxide*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}:\text{CH}\cdot\text{OAc}$ , prepared from acetyl chloride and benzylformhydroxamic acid, melts at  $146$ — $148^{\circ}$ ; the  $\beta$ -modification melts at  $95$ — $96^{\circ}$ , and boils at  $162$ — $163^{\circ}$  under 12 mm. pressure.

*Benzyloximinodiacetyl oxide*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}:\text{CMe}\cdot\text{OAc}$ , results from  $\alpha$ -benzylhydroxylamine and acetic anhydride; it crystallises from petroleum in snow-white needles, and melts at  $101$ — $102^{\circ}$ .

*Benzyloximiniformyl benzoyl oxide*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}:\text{CH}\cdot\text{OBz}$ , obtained from silver benzylformhydroximate and benzoyl chloride, crystallises from petroleum in colourless, transparent plates, and melts at  $29\cdot5$ — $30\cdot5^{\circ}$ ; it dissolves readily in organic solvents, and is resolved by acids into  $\alpha$ -benzylhydroxylamine and formic and benzoic acids. It is also produced when sodium benzylformhydroxamic acid is treated with benzoyl chloride,  $\beta$ -benzoyl- $\alpha$ -benzylhydroxylamine,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NHBz}$ , being also formed; this crystallises in rhombic plates, and melts at  $103$ — $104^{\circ}$  (compare Beckmann, Abstr., 1894, i, 25).

M. O. F.



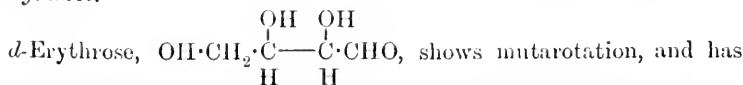
**Purification of Osazones and Estimation of their Rotatory Power.** By CARL NEUBERG (*Ber.*, 1899, 32, 3384—3388).—Practically all osazones are soluble in pyridine, the solubilities of the various members differing but little; as a rule, 1 gram of the solvent dissolves 0.25 gram of an osazone in the cold, and 0.6 gram at the boiling point of the solvent. Most of the osazones may be purified by recrystallisation from a mixture of pyridine and some other suitable solvent, such as water, alcohol, benzene, carbon disulphide, &c., or even more quickly by solution in pyridine and precipitation with benzene, ether, or light petroleum. Hydrazones and hydrazides behave in a similar manner. Solutions of osazones in pyridine or in pyridine and another solvent, especially ethyl alcohol, have been examined polarimetrically. The results obtained differ, not only in amount, but in some cases also in direction, from those given when acetic acid or alcoholic solutions are employed. The following rotations were obtained in a 100 mm. tube by using 0.2 gram of osazone, 4 c.c. of pyridine, and 6 c.c. of ethyl alcohol.

Phenylosazones of *L*-arabinose,  $+1^{\circ}10'$ ; xylose,  $-0^{\circ}15'$ ; rhamnose,  $+1^{\circ}24'$ ; dextrose,  $-1^{\circ}30'$ ; *D*-galactose,  $+0^{\circ}48'$ ; sorbinose,  $-0^{\circ}15'$ ; maltose  $+1^{\circ}30'$ ; lactobiose  $\pm 0^{\circ}$ ; *p*-bromophenylosazones of *L*-arabinose,  $+0^{\circ}28'$ ; xylose,  $\pm 0^{\circ}$ ; dextrose,  $-0^{\circ}31'$ ; *p*-bromophenylhydrazine glycuronate (Abstr., 1899, i, 933) gave  $-7^{\circ}25'$ , from which it follows that  $[\alpha]_D^{20} = -369^{\circ}$ .

*Dextrose p-bromophenylosazone*, melts at  $222^{\circ}$  and resembles the phenylosazone; that of *xylose* melts at  $208^{\circ}$ , and is moderately soluble in most solvents; *L-arabinose-p-bromophenylosazone* sinters at  $185^{\circ}$ , melts at  $196-200^{\circ}$ , and is more readily soluble in ether than the xylose derivative. Most of the parabromophenylosazones crystallise either in the usual yellow needles or in well-developed, six-sided plates.

J. J. S.

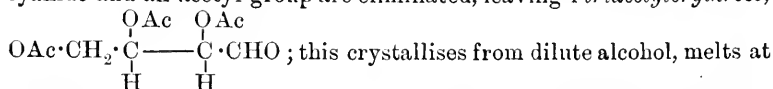
***d*-Erythrose.** By OTTO RUFF [and in part MEUSSER] (*Ber.*, 1899, 32, 3672—3681. Compare Abstr., 1899, i, 324).—Calcium *d*-arabonate, on oxidation with hydrogen peroxide and ferric acetate, yields a mixture rich in *d*-erythrose, which on treatment with phenylbenzylhydrazine gives *d-erythrophenylbenzylhydrazone*; this crystallises in white needles melting at  $105.5^{\circ}$ , has a specific rotation  $[\alpha]_D = -32^{\circ}$  at  $20^{\circ}$ , and on treatment with a solution of formaldehyde yields *d-erythrose*.



an approximate maximum specific rotation  $[\alpha]_D = -14.5^{\circ}$  at  $20^{\circ}$ ; it reduces Fehling's solution slightly in the cold, does not ferment, and yields an *osazone* which crystallises from benzene in the form of yellow needles melting at  $164^{\circ}$ . On reduction with sodium amalgam, it yields inactive erythritol melting at  $120^{\circ}$  (corr.). The melting point of the natural inactive erythritol has been stated by Lamy to be  $112^{\circ}$  and by Liebermann as  $126^{\circ}$ ; the author finds it to be  $120^{\circ}$ . The oxidation of calcium *d*-arabonate with bromine gives *d-erythronic acid*. This is separated by means of the *strychnine* or the *brucine* salt, which

melts about  $215^{\circ}$  and has a specific rotation  $[\alpha]_D -23.5^{\circ}$  at  $20^{\circ}$ . The aqueous solution of the acid, obtained by the decomposition of these salts, turns the plane of polarised light strongly to the left, but on evaporation leaves the *lactone*, which crystallises in the form of compact prisms melting at  $103^{\circ}$  and has a specific rotation  $[\alpha]_D -73.3^{\circ}$  at  $20^{\circ}$ . The *calcium* salt crystallises with  $2H_2O$  and has the specific rotation  $[\alpha]_D +8.2^{\circ}$  at  $20^{\circ}$ . The *phenylhydrazide* forms prismatic leaflets melting at  $128^{\circ}$  and has the specific rotation  $[\alpha]_D +17.5^{\circ}$  at  $20^{\circ}$ . *d*-Erythronic acid is identical with the trihydroxybutyric acid obtained in the oxidation of levulose (Herzfeld, Börnstein, and Winter, Abstr., 1886, 862). R. H. P.

**Degradation of *l*-Arabinose.** By ALFRED WOHL (*Ber.*, 1899, 32, 3666—3672. Compare Abstr., 1893, 292, and 1898, i, 168).—The oxidation and subsequent acetylation of *l*-arabinose yield the nitrile of *l*-tetracetylaronic acid; from this, by the action of silver oxide suspended in methyl alcohol containing a trace of ammonia, hydrogen cyanide and an acetyl group are eliminated, leaving *l*-triacetylerythrose,



On treatment of the nitrile with silver oxide and ammonia, *l*-erythrosediacetamide is obtained; it crystallises from water, melts and decomposes at  $210^{\circ}$ , and has a specific rotation  $[\alpha]_D -7.9^{\circ}$ . On hydrolysis with dilute hydrochloric or sulphuric acid of a solution of the diacetamide, the specific rotation changes to  $[\alpha]_D +32.7^{\circ}$ , which is probably the specific rotation of *l*-erythrose. The sugar could not be crystallised or otherwise purified, but an *osazone* crystallising from benzene or water and melting at  $163$ — $164^{\circ}$  is easily obtained. Attempts were made to purify the sugar from ammonium carbonate by evaporation in a vacuum, but by this means *l*-dierythroseimide,  $NH \left[ CH \begin{smallmatrix} < CH(OH) \\ O-CH_2 \end{smallmatrix} \right]_2 CH \cdot OH$ , is obtained, which crystallises from warm water, melts at  $155^{\circ}$ , exhibits mutarotation, and has a maximum specific rotation  $[\alpha]_D +136.3^{\circ}$ . R. H. P.

**Resolution of Racemic Compounds into Active Components.** By EMIL FISCHER (*Ber.*, 1889, 32, 3617—3619).—The enzyme emulsin hydrolyses the  $\beta$ -methylglucoside of dextrose, but has no action on its optical antipode derived from *l*-glucose; a similar difference is observed when the  $\alpha$ -methyl derivatives are treated with yeast enzymes; under these conditions, the racemic compounds are rendered active, one active form being decomposed whilst the other remains unaltered.

The selective action of enzymes is quite analogous to the partial resolution of *r*-mandelic acid by etherification with *l*-menthol (Marekwald and McKenzie, Abstr., 1899, ii, 733, and Walden, this vol., i, 7). Both processes are similar in principle to the method involving the employment of micro-organisms, but owing to the

substitution of the living cell by an enzyme or by some other asymmetric compound, the phenomenon now becomes a chemical one.

G. T. M.

**Action of Acetic Anhydride on Cellulose in Presence of Sulphuric Acid.** By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1899, 18, 472—476).—A reply to Skraup's note on cellulose (*Abstr.*, 1899, i, 852). The cellulose acetate melting at  $212^{\circ}$  is not identical with inosite hexacetate, which has the same melting point.

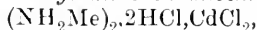
Cellulose acetate is hydrolysed by aqueous ammonia or an ammoniacal solution of cuprous oxide, the cellulose being recovered. It is completely soluble in chloroform, the solution resembling collodion; it also dissolves in acetic acid, and is reprecipitated by the addition of water.

T. H. P.

**Alkalimetry of the Amines.** By A. ASTRUC (*Compt. rend.*, 1899, 129, 1021—1023).—The amines of the aliphatic series behave as strong bases towards phenolphthalein and methyl-orange, whereas the amines of the aromatic series are weak bases, being neutral to phenolphthalein and mono-acid towards methyl-orange. Hydroxylamine behaves as an aromatic amine, its hydrochloride in aqueous solution being neutral to methyl-orange and acid to phenolphthalein. The addition of two aliphatic alkyl groups to a primary aromatic amine does not increase its basicity. When a second phenyl group is introduced into a primary aromatic amine, the basicity is lowered, as is shown by diphenylamine, which is neutral to both phenolphthalein and methyl-orange.

H. R. LE S.

**Double Halogen Salts of Cadmium with the Methylamines and Tetramethylammonium.** By C. D. RAGLAND (*Amer. Chem. J.*, 1899, 22, 417—434).—*Methylamine cadmioclhoride*,



the only double-salt obtainable by mixing solutions of cadmium chloride and methylamine hydrochloride, forms tabular, transparent crystals with a perfect cleavage; of the *bromides*,  $\text{NH}_2\text{Me} \cdot \text{HBr} \cdot \text{CdBr}_2$ , however, is only isolated with difficulty, and forms long, flattened prisms, whilst  $(\text{NH}_2\text{Me})_2 \cdot 2\text{HBr} \cdot \text{CdBr}_2$  separates in large, tabular, crystalline masses; no double iodide could be prepared.

*Dimethylamine cadmioclhorides*.—(1),  $\text{NHMe}_2 \cdot \text{HCl} \cdot \text{CdCl}_2$ , forms long prisms, darkens at  $240^{\circ}$ , and melts and decomposes at  $261$ — $262^{\circ}$ ; (2),  $\text{NHMe}_2 \cdot \text{HCl} \cdot 2\text{CdCl}_2 + 2\text{H}_2\text{O}$  crystallises similarly and does not melt or decompose at  $270^{\circ}$ ; (3),  $(\text{NHMe}_2)_3 \cdot 3\text{HCl} \cdot 2\text{CdCl}_2$ , forms flat, transparent prisms. All three salts are easily soluble in water. *Dimethylamine cadmiobromides*.—(1),  $\text{NHMe}_2 \cdot \text{HBr} \cdot \text{CdBr}_2$  forms slender, white needles or thin prisms; (2),  $(\text{NHMe}_2)_2 \cdot 2\text{HBr} \cdot \text{CdBr}_2$  crystallises in rhombohedral prisms; (3),  $\text{NHMe}_2 \cdot \text{HBr} \cdot 4\text{CdBr}_2$  forms short, thick, brilliant crystals. *Dimethylamine cadmioiodide*,  $\text{NHMe}_2 \cdot \text{HI} \cdot \text{CdI}_2$ , forms tabular, cubical crystals.

*Trimethylamine cadmioclhorides*.—(1),  $\text{NMe}_3 \cdot \text{HCl} \cdot \text{CdCl}_2$  has been described by Hiortdahl (*Zeit. Kryst. Min.*, 1882, 6, 466); (2),  $(\text{NMe}_3)_3 \cdot 3\text{HCl} \cdot 2\text{CdCl}_2$  crystallises in obliquely terminated, flattened prisms. *Trimethylamine cadmiobromides*.—(1),  $\text{NMe}_3 \cdot \text{HBr} \cdot \text{CdBr}_2$

(Hiortdahl, *loc. cit.*); (2),  $(\text{NMe}_3)_3 \cdot 3\text{HBr} \cdot 2\text{CdBr}_2$  forms flattened prisms terminating in pyramidal planes. *Trimethylamine cadmioiodides*.—(1),  $\text{NMe}_3 \cdot \text{HI} \cdot \text{CdI}_2$ , forms large cubes; (2),  $(\text{NMe}_3)_2 \cdot 2\text{HI} \cdot \text{CdI}_2$ , crystallises in beautiful, rhombic prisms.

*Tetramethylammonium cadmiocloride*,  $\text{NMe}_4\text{Cl} \cdot \text{CdCl}_2$ , forms hexagonal-pyramidal crystals. *Cadmibromides*.—(1),  $\text{NMe}_4\text{Br} \cdot \text{CdBr}_2$ , forms crystals similar to those of the corresponding double chloride, and is sparingly soluble in water; (2),  $(\text{NMe}_4\text{Br})_2 \cdot \text{CdBr}_2$ , crystallises in short, imperfect, flattened prisms. *Cadmioiodides*.—(1),  $\text{NMe}_4\text{I} \cdot \text{CdI}_2$  is a crystalline powder sparingly soluble in water; (2),  $(\text{NMe}_4\text{I})_2 \cdot \text{CdI}_2$ , is more easily soluble, and forms transparent octahedra. W. A. D.

**Double Halogen Salts of Tin with Aliphatic Amines and with Tetramethylammonium.** By C. G. COOK (*Amer. Chem. J.*, 1899, 22, 435—446. Compare Slagle, *Abstr.*, 1899, i, 39).—The *stannochloride*,  $\text{NH}_2\text{Me} \cdot \text{HCl} \cdot \text{SnCl}_2$ , of methylamine forms well-defined, transparent prisms, that of *dimethylamine*,  $\text{NHMe}_2 \cdot \text{HCl} \cdot \text{SnCl}_2$ , needle-like crystals, whilst *trimethylamine stannochloride*,  $\text{NMe}_3 \cdot \text{HCl} \cdot \text{SnCl}_2$ , is sparingly soluble in water and crystallises in triangular plates; Hiortdahl's analyses (*Zeit. Kryst. Min.*, 1882, 6, 462) of the stannichlorides of the three bases are confirmed. *Tetramethylammonium stannochloride*,  $\text{NMe}_4\text{Cl} \cdot \text{SnCl}_2$ , is sparingly soluble in water, and from dilute solutions crystallises in needles; it is easily oxidised by the air to the *stannichloride*,  $(\text{NMe}_4\text{Cl})_2 \cdot \text{SnCl}_4$ , which forms measurable crystals.

*Ethylamine stannochloride*,  $\text{NH}_2\text{Et} \cdot \text{HCl} \cdot \text{SnCl}_2$ , forms white needles, and is rapidly oxidised by the air to the *stannichloride*,  $(\text{NH}_2\text{Et})_2 \cdot \text{H}_2\text{SnCl}_6$ , which crystallises in well-defined, pyramidal crystals, possessing little lustre. Trimethylamine stannochloride could not be obtained owing to its rapidly oxidising; specimens of the *stannichloride* were prepared which, although apparently homogeneous, were in reality mixtures of the compounds  $(\text{NMe}_3)_2 \cdot \text{H}_2\text{SnCl}_6$ ;  $\text{NMe}_3 \cdot \text{HCl} \cdot \text{SnCl}_4$ , and  $(\text{NMe}_3)_3 \cdot 3\text{HCl} \cdot \text{SnCl}_4$ .

*Methylamine stannobromide*,  $\text{NH}_2\text{Me} \cdot \text{HBr} \cdot \text{SnBr}_2$ , forms dark-red needles, and the *stannibromide*,  $(\text{NH}_2\text{Me})_2 \cdot \text{H}_2\text{SnBr}_6$ , yellow, crystal masses of varying habit. *Dimethylamine stannobromide*,  $\text{NHMe}_2 \cdot \text{HBr} \cdot \text{SnBr}_2$ , crystallises in beautiful, lustrous, white scales or feathers, and is sparingly soluble in water, whilst the *stannibromide*,  $(\text{NHMe}_2)_2 \cdot \text{H}_2\text{SnBr}_6$ , forms transparent, hexagonal prisms with modified ends. *Trimethylamine stannobromide* could not be prepared owing to its readily oxidising in the air to the *stannibromide*,  $(\text{NMe}_3)_2 \cdot \text{H}_2\text{SnBr}_6$ , which forms small, transparent crystals.

*Ethylamine stannobromide*,  $\text{NH}_2\text{Et} \cdot \text{HBr} \cdot \text{SnBr}_2$ , forms yellowish-white, lustrous needles, and the *stannibromide*,  $(\text{NH}_2\text{Et})_2 \cdot \text{H}_2\text{SnBr}_6$ , bright yellow, transparent, pyramidal prisms. *Triethylamine stannobromide* could not be isolated, but the *stannibromide*,  $(\text{NEt}_3)_2 \cdot \text{H}_2\text{SnBr}_6$ , forms yellow, rhombic plates. W. A. D.

**Physiological Action of Methylnitramine in Relation to its Chemical Constitution.** By G. BELLAAR SPRUYT (*Proc. k. Akad. Wetensch. Amsterdam*, 1899, i, 321—322).—The sodium derivative of methylnitramine has no toxic action on the animal system, and in this respect resembles the nitroparaffins, but differs from the isomeric

nitrites. The physiological behaviour of the substance supports the view of its constitution maintained by Franchimont in opposition to Hantzsch; the former regards it as a nitro-compound (Abstr., 1895, i, 445; compare, however, Abstr., 1897, i, 8; 1898, i, 293), whilst the latter proposes a formula which contains the radicle  $\text{:NO}\cdot\text{OH}$  (compare, however, Abstr., 1896, i, 353, 673), and recalls that of the nitrites.

G. T. M.

**Preparation of Ethyldichloroamine.** By H. PALOMAA (*Ber.*, 1899, 32, 3343—3344. Compare Seliwanoff, Abstr., 1893, i, 192).—Ethyldichloroamine is best prepared by adding a concentrated aqueous solution of ethylamine hydrochloride to dry bleaching powder; the substance thus produced boils at  $85\text{--}90^\circ$  and may be kept under water for 18 months without undergoing decomposition.

G. T. M.

**Preparation of Ethyldichloroamine.** By JOSEPH TCHERNIAC (*Ber.*, 1899, 32, 3582).—The author's method of preparing ethyldichloroamine (Abstr., 1876, i, 913) gives as good results as Palomaa's modification (preceding abstract) of this process; the decomposition of the base on keeping is caused by light and not by the presence of water, and can be prevented by storing in red glass bottles.

W. A. D.

**Stereochemistry of Nitrogen [Propylisobutylamine].** By WILHELM MARCKWALD (*Ber.*, 1899, 32, 3508—3510).—*p*-Toluenesulphopropylamide dissolves readily in organic solvents and melts at  $52^\circ$ . *p*-Toluenesulphopropylisobutylamide crystallises from light petroleum and melts at  $59\text{--}60^\circ$ . Propylisobutylamine boils at  $123^\circ$  under 768 mm. pressure; the hydrochloride melts at  $275^\circ$  and sublimes at a lower temperature; the platinichloride is orange-coloured and melts at  $187\text{--}188^\circ$ ; the aurichloride forms yellow crystals and melts at  $187\text{--}188^\circ$ .

T. M. L.

**Constitution of Lysine.** By ALEXANDER ELLINGER (*Ber.*, 1899, 32, 3542—3546).—Drechsel's lysine, obtained from either casein or the peptone from the self-digestion of the pancreas, gives a fairly good yield of pentamethylenediamine (cadaverine) when allowed to undergo putrefaction by the aid of rotting pancreas in an atmosphere of hydrogen. This would indicate that lysine stands in the same relationship to pentamethylenediamine that ornithine does to tetramethylenediamine (Abstr., 1899, i, 186), and is therefore  $\alpha$ - $\epsilon$ -diaminohexoic acid,  $\text{NH}_2\cdot\text{CH}_2\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ .

J. J. S.

**Derivatives of Pyrotartaric Acid and of the Isomeric Glutaric Acid.** By P. A. MEERBURG (*Rec. Trav. Chim.*, 1899, 18, 367—377).—Pyrotartaric methylamide,  $\text{C}_3\text{H}_6(\text{CO}\cdot\text{NHMe})_2$ , prepared either from methyl pyrotartrate or from pyrotartaric chloride, is found to have the melting point  $164\text{--}165^\circ$ ; the value  $113\text{--}115^\circ$  given by Henry (Abstr., 1885, 886) is hence erroneous.

Pyrotartaric dimethylamide,  $\text{C}_3\text{H}_6(\text{CO}\cdot\text{NMe}_2)_2$ , prepared by the action of dimethylamine on pyrotartaric chloride, is a colourless liquid boiling at  $115\text{--}120^\circ$  under 0.5 to 1 mm. pressure.

*Methyl glutarate*,  $C_3H_6(CO_2Me)_2$ , is a colourless liquid with a faint, pleasant odour; it boils at  $93.5-94.5^\circ$  under 13 mm. and at  $213.5-214^\circ$  under 751.5 mm. pressure. Its specific gravity is 1.09337 at  $15^\circ/4^\circ$ .

*Glutaric methylamide*,  $C_3H_6(CO \cdot NHMe)_2$ , separates by the addition of benzene to its solution in chloroform in large needles melting at  $126^\circ$ ; it is very soluble in water, chloroform, or acetone, less so in benzene, and insoluble in ether or light petroleum.

*Glutaric dimethylamide*,  $C_3H_6(CO \cdot NMe_2)_2$ , is deposited from chloroform in large, transparent, lozenge-shaped crystals, which are very hygroscopic; it melts at  $49-51^\circ$ .

Tables, containing, however, a large number of gaps, are given of the boiling and melting points of derivatives of the acids of the oxalic acid series with odd and even numbers of carbon atoms. The chief regularities shown are as follows: The boiling points of methyl oxalate and succinate differ by  $32^\circ$ , which is also the difference between the values for methyl malonate and glutarate. On replacing a hydrogen atom by methyl in the methyl or ethyl derivatives of these acids, a rise of  $2^\circ$  in the boiling point takes place in the even carbon atom series, whilst in the odd members a fall of  $2^\circ$  is effected. The melting points of the amides of the even terms form a descending series, whilst with the odd members the reverse is the case. The specific gravities of the methyl and ethyl derivatives diminish with an increase in molecular weight in both the odd and even series.

T. H. P.

**Synthesis of Parabanic Acid.** By PAUL CAZENEUVE (*Compt. rend.*, 1899, 129, 834-836).—Parabanic acid is obtained in small quantity by boiling oxamide with phenyl carbonate, and can be identified by its physical properties, and by conversion into calcium oxalurate, and by other chemical reactions.

C. H. B.

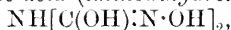
**Constitution and Synthetical Application of Mercury Fulminate.** I. Direct Aldoximation of Benzene. By ROLAND SCHOLL (*Ber.*, 1899, 32, 3492-3501).—Mercury fulminate moistened with benzene (100 grams) is mixed with benzene (150 grams) in a conical flask of  $\frac{1}{2}$ -litre capacity, provided with a delivery tube and a thermometer, which dips into the liquid. Aluminium hydroxide dried for 3 hours at about  $130^\circ$  (15 grams), commercial crystallised aluminium chloride,  $AlCl_3 + 6H_2O$  (15 grams), and freshly prepared, sublimed aluminium chloride (120 grams) are pounded together for  $\frac{1}{4}$  hour in a mortar provided with an india-rubber cap, through which the pestle passes. The mixture in the flask is heated to  $45^\circ$  in a water-bath, and then the aluminium chloride mixture is introduced in portions of 5-10 grams in the course of about 40 minutes, the flask being well shaken all the time. The thermometer is watched and the temperature kept at  $43-45^\circ$  meanwhile, and also for  $\frac{1}{2}-\frac{3}{4}$  hour longer, until it begins to fall of itself. The mixture is allowed to remain for at least 3 hours at the ordinary temperature, pounded in a mortar with crushed ice (700 grams) and concentrated hydrochloric acid (50 c.c.), and extracted with large volumes of ether. The ether is distilled off; mercuric chloride is removed by extracting several times with saturated sodium chloride solution, the benzaldoxime is removed by extraction with 25 per cent. caustic potash, benzaldehyde

with 40 per cent. sodium hydrogen sulphite solution, and benzonitrile by distillation, with or without steam; benzamide remains. About 80 grams of the fulminate enter into the reaction, and the yield of benzaldoxime is about 70 per cent. of the theoretical.

The reaction  $C_6H_6 + C:N \cdot OH = C_6H_5 \cdot CH:N \cdot OH$  is further evidence that fulminic acid is carbonyl oxime (compare Nef., *Abstr.*, 1895, i, 10). The aldoxime is a primary product of the reaction, and so is the nitrile in a sense, resulting probably from the action on the benzene of cyanogen chloride formed from the fulminate; the aldehyde and amide are formed from these. The yield of aldoxime depends on the observance of the details; if pure aluminium chloride is used without admixture of hydroxide or hydrated chloride, the nitrile is the main product. Homologues of benzene and alkoxybenzenes react in the same way as benzene, *m*-dihydroxybenzene derivatives yield aldoximes with the fulminate and hydrogen chloride, without addition of aluminium chloride; presumably monochloroformaldoxime is first formed.

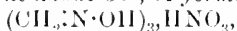
C. F. B.

**Action of Nitric Peroxide on Mercurydimethyl.** By EUGEN BAMBERGER AND JENS MÜLLER (*Ber.*, 1899, 32, 3546—3554).—The oxime of *iminodicarboxylic acid* (*iminodihydroxamic acid*),



is obtained when a perfectly dry ethereal solution of nitric peroxide is slowly added to an ethereal solution of mercurydimethyl, cooled by the aid of a freezing mixture, and kept in constant agitation; it separates as large, colourless needles, which are extremely unstable, and can only be analysed with the greatest difficulty. It dissolves readily in water, yielding an acid solution, but is practically insoluble in ether. It decomposes when warmed by the finger, and explodes violently when dissolved in hydrochloric acid containing a little potassium chlorate in solution. Alkalis dissolve it, yielding a yellow solution smelling slightly of diazomethane, which when acidified and then shaken with ether, imparts a deep blue colour to the ethereal layer; when the ether is evaporated, a colourless, crystalline substance is obtained which possesses the properties of a pseudonitrole, but which has not been further investigated. Mineral acids decompose iminodihydroxamic acid, yielding formic acid, nitrous oxide, hydroxylamine, carbon monoxide and dioxide, ammonia, and probably nitrogen.

An ethereal solution of nitric peroxide reacts with an ethereal solution of formoxime in one of two ways, yielding either clear, glistening plates, which decompose at about 80°, or *formoxime nitrate*,



which crystallises in compact prisms melting at about 120°. The compound decomposing at 80° may be identical with the pseudonitrole derivative mentioned above.

J. J. S.

**Heat of Neutralisation and Acidimetry of Cacodylic Acid.** By HENRI IMBERT (*Compt. rend.*, 1899, 129, 1214—1246).—Cacodylic acid, when dissolved in water, is neutral towards methyl-orange, but towards phenolphthalein it behaves as a monobasic acid. Its heat of neutralisation is 14.10 cal., this value corresponding with the results obtained by Belugon for the action of caustic soda on the acid salts of

the monoalkylphosphates; these compounds, like cacodylic acid, are also neutral to methyl orange and monobasic to phenolphthalein.

G. T. M.

**Cyclic Polymethylenes of [Russian] Petroleum.** By RUDOLF WISCHIN (*Chem. Zeit.*, 1899, 23, 916—926).—A summary and bibliography of the present state of knowledge of the composition of Russian petroleum, and of the naphthenes, naphthylenes, terpenes, and acids of the naphthene series, which either occur in it or have been prepared synthetically.

G. T. M.

**New Compounds of Phosphoric Oxide with Benzene.** By H. GIRAN (*Compt. rend.*, 1899, 129, 964—966. Compare Abstr., 1898, i, 407).—Further examination of the brick-red product obtained (*loc. cit.*) by heating together benzene and phosphoric oxide at 110—120° shows it to be *benzenemonodimetaphosphoric acid*,  $C_6H_5 \cdot P_2O_4 \cdot OH$ ; it is very deliquescent, and is acted on by water with the production of benzene and phosphoric acid. It forms a deep yellow, deliquescent *ammonium* salt,  $P_2O_5PhNH_4$ , which is decomposed by water, yielding *ammonium* phosphate and benzene; the *sodium* and *potassium* salts form yellow precipitates rapidly decomposed by water.

At higher temperatures (200—210°), benzene and phosphoric anhydride combine to form *benzenetridimetaphosphoric acid*,  $C_6H_5 \cdot 3P_2O_5 = C_6H_3(P_2O_4 \cdot OH)_3$ , which is a yellow, deliquescent substance slightly soluble in alcohol, insoluble in benzene, ether, carbon disulphide, or chloroform, and is decomposed by water. The *ammonium* salt,  $C_6H_3(P_2O_5NH_4)_3$ , is a light yellow substance.

T. H. P.

**Constitution of  $\alpha$ -Dibromodinitrobenzene.** By D. F. CALHANE and P. M. WHEELER (*Amer. Chem. J.*, 1899, 22, 449—458).—Austen's " *$\alpha$ -dibromodinitrobenzene*" (Abstr., 1876, ii, 406), on reduction with zinc dust and acetic acid, yields 3:6-dibromo-*o*-phenylenediamine, which, on distillation with steam, is obtained in felted, slender, white needles melting at 94—95°; it cannot be crystallised from hot water, as it is thereby partially decomposed. The *hydrochloride* forms white, lustrous needles, and is decomposed on heating, either alone or with water; the *diacetyl* derivative,  $C_6H_3Br_2(NHAc)_2$ , crystallises from hot alcohol in white, thread-like, matted crystals, and melts and decomposes at 265—269°. The base is converted by further reduction with sodium amalgam into *o*-phenylenediamine, and condenses with phenanthraquinone to form *p*-dibromophenanthraphenazine or *phenanthra-p*-dibromophenoquinoxaline,  $C_{20}H_{10}N_2Br_2$ , which crystallises from benzene in concentric aggregates of silky, yellow needles; with benzil, 5:8-dibromo-2:3-diphenylquinoxaline,  $C_{20}H_{12}N_2Br_2$ , crystallising in sheaf-like aggregates of needles and melting at 215—216°, is obtained.

These facts show that Austen's dinitro-compound is 1:4-dibromo-2:3-dinitrobenzene.

W. A. D.

**Rate of Substitution of a Nitro-group by an Alkoxy.** By CORNELIS A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, 1, 144—148. Compare Abstr., 1899, i, 744—747).—A discussion of results already published.

G. T. M.



**Phenyl- and *p*-Chlorophenyl-nitromethane.** By A. VAN RAALTE (*Rec. Trav. Chim.*, 1899, 18, 378—407).—The boiling point curve of mixtures of *p*-chlorotoluene and *p*-chlorobenzyl chloride rises continuously between 158° and 215°; so that, in preparing *p*-chlorobenzyl chloride by the action of chlorine on boiling *p*-chlorotoluene, the reaction is complete when the temperature of the boiling liquid reaches 215°.

*p*-Chlorobenzyl iodide,  $C_6H_4Cl \cdot CH_2I$ , prepared by the action of potassium iodide on the corresponding chloride, is soluble in ether or alcohol, and crystallises from the latter in colourless needles melting at 64°, which smell something like aniseed, and strongly attack the mucous membranes of the eyes and nose. By acting on the iodide with silver nitrite, *p*-chlorophenylnitromethane [*p*-chloro-*o*-nitrotoluene],  $C_6H_4Cl \cdot CH_2 \cdot NO_2$ , is obtained; this compound exists in two modifications, the normal form melting at 33—34°. The *iso*-compound,  $C_6H_4Cl \cdot CH \cdot NO \cdot OH$ , which melts at 64°, gradually changes into the normal form, the melting point passing through a minimum of about 28°. In phenol solution, both modifications give the normal depression of freezing point; in acetic acid, the *iso*-compound has the normal molecular weight, whilst in diphenylmethane the mean value obtained is 208.5 instead of 171.5. The normal modification acts like a pseudo-acid, dissolving only slowly in caustic alkali solution; further, it gives no reaction with ferric chloride, forms a neutral aqueous solution, and a *N*/50 solution in a mixture of equal parts of methyl alcohol and water is a bad conductor of electricity. The *iso*-compound, on the other hand, acts as an acid, as it dissolves readily in sodium carbonate solution, gives a deep coloration with ferric chloride, and forms an acid aqueous solution; it also has a high conductivity which, however, falls as the *iso*-form becomes converted into the normal compound.

Acetylbenzhydroxamic acid,  $COPh \cdot NH \cdot OAc$ , obtained by the action of acetyl chloride on either sodium phenylnitromethane or benzhydroxamic acid, forms small, white needles melting at 125—126°.

*p*-Chlorobenzoylbenzhydroxamic acid,  $COPh \cdot NH \cdot O \cdot CO \cdot C_6H_4Cl$ , prepared by the action of *p*-chlorobenzoyl chloride on benzhydroxamic acid, separates from benzene in colourless crystals melting at 137°.

*p*-Chlorobenzhydroxamic acid,  $C_6H_4Cl \cdot CO \cdot NH \cdot OH$ , crystallises in small, shining plates melting at 168°, and *p*-dichlorodibenzhydroxamic acid,  $C_6H_4Cl \cdot CO \cdot NH \cdot O \cdot CO \cdot C_6H_4Cl$ , when crystallised from acetic acid, melts at 165°.

Benzoyl-*p*-chlorobenzhydroxamic acid,  $C_6H_4Cl \cdot CO \cdot NH \cdot O \cdot Bz$ , when deposited from benzene solution, melts at 158°. T. H. P.

**Separation of Primary, Secondary, and Tertiary Amines by Ginsberg's Method.** By WASSILY SOLONINA (*Chem. Centr.*, 1899, ii, 867—868; from *J. Russ. Chem. Soc.*, 1899, 31, 640—655. Compare *ibid.*, 29, 404).—The investigation of the action of benzenesulphonic chloride, and in some cases of *p*-bromobenzenesulphonic chloride and *m*-nitrobenzenesulphonic chloride on eleven primary amines of the fatty, and on five of the aromatic series, shows that Ginsberg's method of separating primary and secondary amines, which depends

on the different solubility of the products of these reactions, is in many cases inapplicable.

Of the following compounds, those of the type  $\text{NHR} \cdot \text{SO}_2\text{Ph}$  are soluble in alkalis, except where it is stated to the contrary, whilst those of the type  $\text{NR}(\text{SO}_2\text{Ph})_2$  are insoluble; the compounds of both classes are usually easily soluble in hot alcohol, ether, or benzene.

By the action of benzenesulphonic chloride on butylamine in presence of potassium hydroxide, *benzenesulphonbutylamide*,  $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$ , and *dibenzenesulphonbutylamide*,  $\text{C}_4\text{H}_9 \cdot \text{N}(\text{SO}_2\text{Ph})_2$ , are formed. The former is an oil which is insoluble in water, and when treated with nitric acid of sp. gr. 1.48 forms *benzenesulphonbutylnitramide*,  $\text{C}_4\text{H}_9 \cdot \text{N}(\text{NO}_2) \cdot \text{SO}_2\text{Ph}$ , which crystallises in colourless plates, melts at  $29^\circ$ , is insoluble in water or alkalis, but easily soluble in alcohol, ether, or benzene. *Dibenzenesulphonbutylamide* crystallises in plates, melts at  $89-90^\circ$ , and is insoluble in water and slightly soluble in cold alcohol. *p-Bromobenzenesulphonbutylamide* melts at  $58^\circ$  and yields a *nitramide* which melts at  $37-38^\circ$ . *Di-p-bromobenzenesulphonbutylamide* melts at  $116^\circ$  and is slightly soluble in cold alcohol. *m-Nitrobenzenesulphonbutylamide* is crystalline, melts at  $69-70^\circ$ , and by the action of nitric acid yields the *nitramide*, which is crystalline, melts at  $80-81^\circ$ , and is insoluble in water or alkalis. *Di-m-nitrobenzenesulphonbutylamide* is crystalline, melts at  $136^\circ$ , and is insoluble in water. By the action of benzenesulphonic chloride on propylamine, *benzenesulphonpropylamide*,  $\text{NHPr} \cdot \text{SO}_2\text{Ph}$ , is formed, together with a small quantity of a compound which melts at  $65^\circ$ , is insoluble in alkalis, and probably consists of *dibenzenesulphonpropylamide*. The former forms white crystals, melts at  $36^\circ$ , and by the action of nitric acid yields the *nitramide*, which melts at  $34-35^\circ$ . When *p-bromobenzenesulphonic chloride* acts on propylamine, *di-p-bromobenzenesulphonpropylamide*, melting at  $27^\circ$ , is formed in small quantity together with *p-bromobenzenesulphonpropylamide*, which forms white crystals, melts at  $65^\circ$ , is insoluble in water, and by the action of nitric acid yields the *propylnitramide*, which melts at  $44^\circ$ . *Dibenzenesulphonmethylethylamide*,  $\text{NMe}(\text{SO}_2\text{Ph})_2$ , melts at  $104-105^\circ$ . Ethylamine under similar conditions forms only *benzenesulphonethylethylamide*. *p-Bromobenzenesulphonethylethylamide* melts at  $81^\circ$ , the *di-p-bromobenzenesulphonethylethylamide* at  $132^\circ$ . By the action of benzenesulphonic chloride on  $\beta$ -aminobutane, *benzenesulphonpseudobutylamide*, melting at  $70.5^\circ$ , is alone formed. *p-Bromobenzenesulphonpseudobutylamide* melts at  $80^\circ$ . *m-Nitrobenzenesulphonpseudobutylamide*,  $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , melts at  $58^\circ$ . *Benzenesulphonisopropylamide* melts at  $26^\circ$ , and *p-bromobenzenesulphonisopropylamide* at  $99.5^\circ$ . The corresponding *nitramides* melt at  $35^\circ$  and  $82-83^\circ$ . *Benzenesulphonvalerylamide*, prepared from  $\beta$ -aminopentane, is insoluble in water and melts at  $40^\circ$ .  $\epsilon$ -Amino- $\alpha$ -hexylene forms only *benzenesulphonhexylamide* melting at  $36.5-37^\circ$ . *Benzenesulphonallylamide*, prepared from allylamine, melts at  $39-40^\circ$ .

By the action of benzenesulphonic chloride on aniline and *m*-xylylidine, compounds of the type  $\text{NHR} \cdot \text{SO}_2\text{Ph}$  soluble in alkalis are formed. When an excess of the acid chloride is used, or by the action of the chloride on the preceding compounds in presence of alkali, small

quantities of the compounds  $\text{NR}(\text{SO}_2\text{Ph})_2$  are produced. *Dibenzenesulphonanilide*,  $\text{NPh}(\text{SO}_2\text{Ph})_2$ , forms white crystals and melts at  $128-129^\circ$ . The *benzoyl* derivative,  $\text{NPhBz}\cdot\text{SO}_2\text{Ph}$ , crystallises in needles and melts at  $112-113^\circ$ . *Benzenesulphon-m-xylide* forms prismatic crystals and melts at  $130-131^\circ$ . *Dibenzenesulphon-m-xylide*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}(\text{SO}_2\text{Ph})_2$ , crystallises in small needles and melts at  $142^\circ$ .

*Benzenesulphonheptylamide*,  $\text{C}_7\text{H}_{15}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ , differs from the preceding compounds of the same type in being insoluble in alkalis. *Dibenzenesulphonheptylamide* forms leaf-like crystals, melts at  $91^\circ$ , and is insoluble in alkalis. *a*-Camphylamine yields *benzenesulphon-a-camphylamide*, which is a viscous oil and is also insoluble in alkalis. *Dibenzylsulphoncamphylamide*,  $\text{C}_{10}\text{H}_{17}(\text{SO}_2\text{Ph})_2$ , is also formed, but could not be isolated. *p*-Bromobenzenesulphonic chloride and *m*-nitrobenzenesulphonic chloride react in a similar manner to benzenesulphonic chloride. *Benzenesulphonisoundecylamide*, prepared from  $\beta$ -aminoundecane, melts at  $64-65^\circ$  and is insoluble in alkalis, but soluble in alcohol, ether, or benzene. Aminomenthone yields a sulphobenzene derivative,  $\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ , which melts at  $82-85^\circ$  and is soluble in alkalis. No definite compounds could be isolated from the products of the action of benzenesulphonic chloride on diaminohexahydrocymene. Details of a crystallographic examination of dibenzenesulphonbenzylamide are given in the original paper.

E. W. W.

**Behaviour of Sulphonamides of Primary Amines towards Alkalis.** By WILHELM MARCKWALD (*Ber.*, 1899, 32, 3512—3513. Compare Abstr., 1899, i, 749, and Solonina, preceding abstract).—Benzenesulphonheptylamide does not dissolve in dilute sodium hydroxide (compare Solonina), but is nevertheless partly converted into the sparingly soluble sodium salt, which solidifies when shaken with strong sodium hydroxide, and can be recrystallised from acetone. Hinsberg's rule therefore holds good, but, as in other cases, the salt is partially hydrolysed by water.

T. M. L.

**Fixation of Sodium Hydrogen Sulphite by Ethylene Linkings.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1077—1080).—It would appear from Tiemann's researches on aldehydes and ketones that the fixation of sodium hydrogen sulphite by an ethylene linking generally should depend largely on the characteristic function of the molecule, and a series of experiments was made with various typical substances in order to ascertain whether this was the case. When styrene is boiled for 10 hours in a reflux apparatus with excess of sodium hydrogen sulphite solution, only traces of an organic salt are formed, but cinnamyl alcohol under the same conditions yields a notable quantity of a white, deliquescent, very soluble salt of the composition  $\text{C}_9\text{H}_{11}\text{O}_4\text{SNa}$ . Geraniol and citronellol form similar compounds of the composition  $\text{C}_{10}\text{H}_{19}\text{O}_7\text{S}_2\text{Na}_2$  and  $\text{C}_{10}\text{H}_{21}\text{O}_4\text{SNa}$  respectively; in the case of geraniol, the yield is about 15 per cent. With cinnamic acid, the reaction occurs much more readily, a large yield of the compound  $\text{C}_9\text{H}_8\text{O}_5\text{SNa}_2$  being obtained; this salt is, however, difficult to separate on account of its very sparing solubility in

alcohol. It is concluded that the fixation of sodium hydrogen sulphite by an ethylene linking takes place with great difficulty in the case of aromatic hydrocarbons with an aliphatic side-chain, but more readily in the case of alcohols, especially aliphatic alcohols of the type of geraniol, whilst with acids, probably because of their solubility, combination occurs with great ease. N. L.

**Resin Oil.** By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1899, 32, 3614).—The oil obtained by distilling colophony under pressure (*Ber.* 1899, 32, 2952), to which the authors assigned the formula  $C_{42}H_{62}$ , appears, from a determination of its molecular weight by the cryoscopic method, to have the composition  $C_{15}H_{28}$ , and is perhaps derived from abietic acid by the loss of 1 mol. of carbon dioxide.

W. A. D.

**Conversion of 1:8- and 1:5-Dinitronaphthalenes into Nitro-nitrosonaphthols.** By PAUL FRIEDLÄNDER (*Ber.*, 1899, 32, 3528—3532. Compare Graebe, this vol., i, 24).—If the action of sulphuric acid on dinitronaphthalene is continued until the product is completely soluble in alkali, sulphonation occurs; the sulphonic acids are converted on nitration into trinitronaphthols identical with those produced on nitrating the nitronitrosonaphthol, which forms the chief product of the action, and are therefore 8- or 5-nitro-4-nitroso-1-naphthol-3-sulphonic acids. 8-Nitro-4-nitroso-1-naphthol gives a *benzoate* which crystallises from xylene in yellowish-white, slightly soluble needles and melts at  $194^{\circ}$ , whilst the 5:4-derivative gives a similar *benzoate* which melts at  $210^{\circ}$ . The nitronitrosonaphthols are converted by alkaline potassium ferricyanide into the potassium salts of the corresponding dinitronaphthols; 4:5-dinitro-1-naphthol crystallises in straw-yellow needles and melts at  $230^{\circ}$ , whilst 4:8-dinitro-1-naphthol melts at  $135^{\circ}$ ; the dinitronaphthols have only feeble dyeing properties but give trinitronaphthols which resemble naphthol yellow in this respect.

4:8-Diamino-1-naphthol is oxidised by cold ferric chloride to a blue solution of the quinoneimide, but, on warming, to a red solution of 5-amino- $\alpha$ -naphthaquinone, which crystallises from acetic acid, melts and decomposes at about  $180^{\circ}$ , and dissolves in sulphuric acid to a colourless, crystalline salt.

1:3-Dinitronaphthalene is not produced in the nitration of nitronaphthalene by nitrosulphuric acid; the 1:5- and 1:8-dinitronaphthols can be very readily separated by crystallising from pyridine instead of extracting with acetone; by using suitable quantities of sulphuric acid in the nitration, a similar separation can be effected, the whole of the 1:5-dinitronaphthalene crystallising out on cooling, whilst the 1:8-dinitronaphthalene remains in solution, and can be converted directly, if desired, into 1:3:8-trinitronaphthalene by adding a further amount of nitric acid.

1:3:8-Trinitronaphthalene dissolves in cold sodium hydrogen sulphite to a red solution of an additive compound, from which it is precipitated unchanged by warming with acids. T. M. L.

**Fittig's Reaction.** By MICHEL PELLEGRIN (*Rec. Trav. Chim.*, 1899, 18, 457—465).—By the action of sodium on a mixture of *m*-xylylene dibromide and bromobenzene, three definite products were obtained. 1. Diphenyl. 2. *m*-Dixylylene (?),  $C_{16}H_{16}$ , slightly soluble in alcohol or ether and crystallising from the latter in hexagonal prisms melting at  $131.5^{\circ}$ ; cryoscopic determinations in benzene gave a mean molecular weight 205.5,  $C_{16}H_{16}$  requiring the number 208. It boils at  $170^{\circ}$  under 12 mm. and at  $290^{\circ}$  under the ordinary pressure, and forms a dibromo-derivative,  $C_{16}H_{14}Br_2$ , crystallising from benzene in colourless prisms which melt at  $213$ — $214^{\circ}$ . 3. *Di-m-phenylene-diethene* (?),  $C_6H_4 \begin{smallmatrix} <CH:CH> \\ <CH:CH> \end{smallmatrix} C_6H_4$ , which crystallises from a mixture of ether and alcohol in long, silky, colourless needles, melts at  $191^{\circ}$ , boils at  $260^{\circ}$  under 12 mm. pressure, and is very soluble in ether, but less so in alcohol, benzene, or carbon disulphide. In freezing benzene, it has the mean molecular weight 200.9, the value for  $C_{16}H_{12}$  being 204.

The only definite product obtained by the action of sodium on a mixture of *m*-bromobenzene and benzyl chloride was dibenzyl.

T. H. P.

**Synthesis of Picene.** By T. HIRN (*Ber.*, 1899, 32, 3341—3343. Compare Abstr., 1892, 623, and 1895, i, 292).—Picene is a phenanthrene of the naphthalene series and contains a linking joining the two naphthalene residues in the  $\beta\beta'$ -position. The exact position of the dimethenyl group is, however, not known with certainty, and accordingly three formulæ for picene are possible; it may be an  $\alpha\beta\alpha'\beta'$ -, a  $\beta\beta'\beta'\beta'$ - or an  $\alpha\beta\beta'\beta'$ -derivative. The first of these constitutions is the most probable, because the hydrocarbon is produced when *aa'*-dinaphthastilbene (Abstr., 1893, 272) is distilled through a red hot glass tube. The properties of the product correspond with those of picene from coal-tar, except that the xylene solution of the former is not fluorescent.

G. T. M.

**Double Halogen Salts of Tin with Organic Bases.** By GEORGE M. RICHARDSON and MAXWELL ADAMS (*Amer. Chem. J.*, 1899, 22, 446—449).—In addition to the compounds obtained by Slagle (Abstr., 1899, i, 39), the following have been prepared. *Tetraniline stannichloride*,  $(NH_2Ph)_4, 4HCl, SnCl_4$ , is obtained in well-formed crystals. *Dimethylaniline stannochloride*,  $NMe_2Ph, HCl, SnCl_2 + \frac{1}{2}H_2O$ , corresponds in preparation and crystalline form with Slagle's analogous toluidine compounds.

*Aniline stannobromide*,  $NH_2Ph, HBr, SnBr_2$ , forms small, white, spear-like crystals, which melt at  $152^{\circ}$ , and become oxidised on being recrystallised. *Dianiline stannibromide*,  $(NH_2Ph)_2, H_2SnBr_6$ , forms flat, tabular, straw-coloured crystals, whilst *tetraniline stannibromide*,  $(NH_2Ph)_4, 4HBr, SnBr_4$ , which is less soluble in water than the dianiline compound, separates in light-yellow, well-formed crystals, and melts and decomposes at  $274^{\circ}$ .

W. A. D.

**Anilides.** By FREDERICK D. CHATTAWAY, KENNEDY J. P. ORTON, and W. H. HURTLEY (*Ber.*, 1899, 32, 3635—3638. Compare Trans., 1899, 75, 1046, and following abstract).—The following anilides have

been obtained by the transformation of substituted nitrogen chlorides or bromides.

*p*-Chloroformylanilide, obtained from the isomeric phenylformyl-nitrogen chloride, crystallises in white plates and melts at 102°.

2:4-Dichloroformylanilide, prepared either from the corresponding nitrogen chloride or by formylating 2:4-dichloroaniline, crystallises from alcohol in white needles melting at 154°; the benzoyl derivative forms white prisms and melts at 115°.

2:4:6-Trichloroformylanilide crystallises from alcohol or chloroform in white needles and melts at 186°; the acetyl derivative is most conveniently prepared from acetyl-2:4-dichlorophenylnitrogen chloride; the benzoyl derivative crystallises from alcohol in white needles melting at 174°.

2:4-Dibromoformylanilide forms lustrous, white needles melting at 145°; the acetyl derivative is readily prepared from the isomeric acetyl-*p*-bromophenylnitrogen bromide.

2:4:6-Tribromoformylanilide, crystallises in white needles and melts at 221.5°; the acetyl derivative is easily obtained from acetyl-2:4-dibromophenylnitrogen bromide.

1-Chloro-2-formylnaphthalide crystallises from benzene in prisms melting at 136°. G. T. M.

**Substituted Nitrogen Bromides and their Relationship to Bromo-substituted Anilides and Anilines.** By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1899, **32**, 3573—3582. Compare *Trans.*, 1899, **75**, 1046).—Substituted nitrogen bromides of the type  $R \cdot CO \cdot NBrR'$  are readily obtained by the action of hypobromous acid on the corresponding anilides. They are all sulphur-yellow compounds of low melting point, crystallising from light petroleum either in large, transparent prisms or in plates, and are characterised by the readiness with which they enter into various chemical reactions. They react with hydrobromic acid, hydrocyanic acid, potassium iodide solution, or hydrogen peroxide, regenerating the original anilide. They are much more easily hydrolysed than the corresponding chlorides (*loc. cit.*), and are readily decomposed by alcohol, yielding the anilide, together with ethyl bromide, acetaldehyde, and ethyl acetate. When heated, all these nitrogen bromide derivatives undergo molecular transformation, the bromine atom migrating from the nitrogen to a carbon atom of the benzene nucleus, always in the para-position unless this is already occupied, when an ortho-derivative is formed. The authors conclude that in the ordinary bromination of an aniline or anilide the bromine becomes first attached to the nitrogen atom and then passes to the benzene nucleus.

Acetylphenylnitrogen bromide (*N*-bromoacetylanilide, acetylphenylbromamide),  $NPhBrAc$ , obtained by the action of hypobromous acid on a cold saturated solution of acetylanilide at 0° containing potassium hydrogen carbonate, melts at 88°, is readily soluble in chloroform, but only moderately so in light petroleum; when kept for any length of time, it gradually becomes transformed into *p*-bromoacetanilide.

Acetyl-*p*-bromophenylnitrogen bromide,  $C_6H_4Br \cdot NBrAc$ , crystallises in

six-sided plates melting at  $108^{\circ}$ ; the isomerisation is not complete even after the bromide has been kept for some months. The 2:4-dibromo-derivative melts at  $110^{\circ}$ , and is quite stable at the ordinary temperature. The 2:4:6-tribromo-derivative melts at  $123^{\circ}$ , and when strongly heated gives up bromine and forms 2:4:6-tribromoacetylanilide. *Formylphenylnitrogen bromide*,  $\text{NPhBr}\cdot\text{CHO}$ , melts at  $88\text{--}89^{\circ}$ , and when allowed to remain for 24 hours is completely transformed into *p*-bromoformylanilide. The *p*-bromo-derivative melts at  $113^{\circ}$ ; the 2:4-dibromo-derivative melts at  $87^{\circ}$  and the 2:4:6-tribromo-derivative at  $90^{\circ}$ . *Benzoylphenylnitrogen bromide* (*N*-bromobenzoylanilide, *benzoylphenylbromamide*),  $\text{NBrPhBz}$ , is best obtained by allowing an alcoholic solution of benzoylanilide to drop slowly into an excess of hypobromous acid containing potassium hydrogen carbonate in solution at  $0^{\circ}$ ; it crystallises in small, yellow plates melting at  $99^{\circ}$ , and is readily transformed into benzoyl-*p*-bromophenylnilide. The *p*-bromo-derivative melts at  $132\text{--}133^{\circ}$ ; the 2:4-dibromo-derivative melts and decomposes at  $121^{\circ}$ ; and when heated for half an hour at  $100^{\circ}$  yields 2:4:6-tribromobenzoylanilide melting at  $198^{\circ}$ . The 2:4:6-tribromo-derivative melts at  $121^{\circ}$ . J. J. S.

**Symmetrical Dinitrodixylylcarbamides and Dinaphthylcarbamides.** By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 948—951).—These compounds have been prepared by methods similar to those employed for the preparation of the dinitrodiphenylcarbamides and the dinitroditolylcarbamides (Abstr., 1899, i, 692, 810), namely, by heating the isomeric nitroxylidines and naphthylamines with carbonyl chloride or phenyl carbonate.

*Dinitrodixylylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NO}_2)_2$  [ $\text{NH}:\text{Me}_2:\text{NO}_2=4:1:3:5$ ], from 5-nitro-1:3:4-*m*-xylylidine, crystallises from anhydrous acetic acid in small, yellow needles, subliming without melting at about  $300^{\circ}$ , and is insoluble in water, benzene, ether, or chloroform. Like other compounds in which the  $\text{NO}_2$  and  $\text{NH}_2$  groups occupy the ortho-position with regard to each other, 5-nitro-1:3:4-*m*-xylylidine reacts with carbonyl chloride, but not with phenyl carbonate.

*Dinitrodixylylcarbamide* [ $\text{NH}:\text{Me}_2:\text{NO}_2=4:1:3:6$ ] is only obtained in very small quantity by the general methods indicated above, and is best prepared by the action of 6-nitro-1:3:4-*m*-xylylidine on 6-nitro-1:3:4-*m*-xylylcarbimide in benzene solution. It crystallises in microscopic, white needles which sublime without melting when heated, and is insoluble in water, benzene, ether, and chloroform.

$\alpha$ - and  $\beta$ -*s*-Dinaphthylcarbamides, prepared by this method, were found to melt at  $314\text{--}315^{\circ}$  and  $309\text{--}310^{\circ}$  respectively, not at  $270^{\circ}$  and  $293^{\circ}$  as previously stated.

[Young and Clark (Trans., 1897, 71, 1200, give the melting points at  $284\text{--}286^{\circ}$  and  $289\text{--}290^{\circ}$ ]. N. L.

**Aromatic Carbimides.** By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 952—958).—The following new compounds have been obtained by the action of carbonyl chloride on aromatic bases, according to the general method which has been recently described (Abstr., 1899, i, 756).

*5-Nitro-m-xylylcarbimide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2 \cdot \text{N} : \text{CO}$  [ $\text{Me}_2 : \text{N} : \text{CO} : \text{NO}_2 = 1 : 3 : 4 : 5$ ], from 5-nitro-1 : 3 : 4-*m*-xylidine, crystallises in microscopic, yellow needles melting at  $71-72^\circ$  and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

*Ethyl 5-nitro-m-xylylcarbamate* [ $\text{Me}_2 : \text{NH} \cdot \text{CO}_2\text{Et} : \text{NO}_2 = 1 : 3 : 4 : 5$ ] formed by the interaction of alcohol and the preceding compound, crystallises from 95 per cent. alcohol in small, amber-yellow prisms melting at  $125-126^\circ$ ; it is soluble in chloroform.

*6-Nitro-1 : 3 : 4-m-xylylcarbimide*, from 6-nitro-1 : 3 : 4-*m*-xylidine, crystallises in large, yellow needles melting at a few degrees above zero and distilling without decomposition at  $212-214^\circ$  under 97 mm. pressure.

*Ethyl 6-nitro-1 : 3 : 4-m-xylylcarbamate*, obtained by the action of alcohol on the preceding compound, crystallises from alcohol in large, white needles melting at  $120^\circ$ ; it is insoluble in cold, but soluble in boiling water.

*p-Chlorophenylcarbimide*, from *p*-chloroaniline and carbonyl chloride, is a white, crystalline substance which melts at  $30-31^\circ$  to a colourless liquid having a very irritating odour.

*Ethyl p-chlorophenylcarbamate*, prepared by treating the corresponding carbimide with alcohol, crystallises in white, silky plates melting at  $68^\circ$ , and is very soluble in ether, benzene, or chloroform.

*m-Chlorophenylcarbimide*, from *m*-chloroaniline, is a colourless liquid of irritating odour which boils at  $113-114^\circ$  under 43 mm. pressure.

*Ethyl m-chlorophenylcarbamate*, from the corresponding carbimide and alcohol, is an unstable, viscous, colourless liquid which boils at  $200-201^\circ$  under 46.5 mm. pressure.

*o-Chlorophenylcarbimide*, from *o*-chloroaniline, is a colourless liquid boiling at  $114-115^\circ$  under 43 mm. pressure and having a very irritating odour.

*Ethyl o-chlorophenylcarbamate*, from the preceding compound and alcohol, is a colourless liquid which boils at  $170-172^\circ$  under 42 mm. pressure.

*p-Iodophenylcarbimide*, from *p*-iodoaniline, is a crystalline substance of agreeable odour melting at  $45-46^\circ$ ; it is very unstable and quickly decomposes, yielding the corresponding carbamide.

*Ethyl p-iodophenylcarbamate* crystallises in large, white needles melting at  $111-112^\circ$  and is very soluble in ether, benzene, or chloroform.

*p-Methoxyphenylcarbimide*, from *p*-anisidine, is a colourless liquid which quickly becomes yellow and decomposes; it boils at  $132-133^\circ$  under 38.5 mm. pressure.

*Ethyl p-methoxyphenylcarbamate* crystallises in large, white needles melting at  $63-64^\circ$ ; it is very soluble in ether, chloroform, or benzene.

$\alpha$ -Naphthylcarbamide, from  $\alpha$ -naphthylamine, is a brown liquid having a very irritating odour. Ethyl  $\alpha$ -naphthylcarbamate crystallises in small, white needles melting at  $79^\circ$ . This and the preceding compound have been previously obtained by Hofmann by other methods.

$\beta$ -Naphthylcarbimide, from  $\beta$ -naphthylamine, crystallises from light



petroleum in white plates melting at 55—56° and is very soluble in ether or benzene.

*Ethyl β-naphthylcarbamate*, obtained by the action of alcohol on the corresponding carbimide crystallises from 40 per cent. alcohol in small, white needles melting at 69°; it is very soluble in ether, benzene, chloroform, or 95 per cent. alcohol. N. L.

**Characteristics of Stereoisomeric Ammonium Salts.** By EDGAR WEDEKIND (*Ber.*, 1899, 32, 3561—3569. Compare Abstr., 1899, i, 351, and Pope and Peachey, *Trans.*, 1899, 75, 1127).—*α*- (or *γ*)-*Phenylbenzylmethylallylammonium bromide* is obtained by the direct combination of benzylmethylaniline and allyl bromide or more readily of methylallylaniline and benzyl bromide; it melts and decomposes not very sharply at 161—163°, and dissolves readily in warm alcohol or water, but when its aqueous solution is boiled, decomposition ensues; it crystallises in the rhombic system and is isomorphous with the *α*-iodide (*loc. cit.*) [*a* : *b* : *c* = 0.88888 : 1 : 0.65854]. The *α*-chloride is obtained when the *α*-iodide is treated with moist silver oxide, then with concentrated hydrochloric acid, and the solution thus formed evaporated at 50—60°; it crystallises in large, spear-shaped, rhombic crystals isomorphous with the *α*-bromide and *α*-iodide, melts at 152—154°, and is readily soluble in most organic solvents with the exception of light petroleum and ether; it also dissolves in water, but the solution, when boiled, undergoes partial hydrolysis. The *platinichloride*, (C<sub>17</sub>H<sub>20</sub>N)<sub>2</sub>PtCl<sub>6</sub>, crystallises in minute, yellow needles and the *aurichloride* forms a yellow, amorphous powder melting at 90—94°.

*β*-*Phenylbenzylmethylallylammonium bromide* is obtained when benzylallylaniline and pure methyl bromide are left in contact with one another for several months at the ordinary winter temperature. It crystallises from a mixture of chloroform and acetone in well-developed, colourless, monoclinic plates, is specifically heavier and also melts at a lower temperature, namely, 105—107°, than the isomeric bromide. It is apparently hemihedral [*a* : *b* : *c* = 1.1128 : 1 : 1.3084; *β* = 71°45′]. The *β*-chloride, obtained indirectly from either the bromide or iodide, crystallises in small, glistening, monoclinic prisms isomorphous with the *β*-bromide [*a* : *b* : *c* = 1.054 : 1 : 1.260; *β* = 71°40′]. It decomposes at 113—116° whereas the *α*-chloride decomposes at 152—154°. The *β*-iodide (*loc. cit.*) is not isomorphous with the *β*-chloride and bromide; as it crystallises in the rhombic system; it may, however, be dimorphous. The *platinichloride* crystallises in brownish-yellow needles decomposing at 198—199°; the *β*-aurichloride forms golden-yellow needles melting at 105—107° and decomposing at about 180°. Both compounds are more soluble than the isomeric *α*-derivatives.

J. J. S.

**Acyl Derivatives of the Aromatic Thiocarbamides: their Isomerism and Constitution.** By A. HUGERSHOFF (*Ber.*, 1899, 32, 3649—3660).—Acyl derivatives of the aromatic thiocarbamides can be prepared by dissolving the carbamide in the acyl anhydride at about 80°, and allowing the solution to remain for some time at the ordinary temperature, whereas, if the solution is heated, decomposition occurs, and thiocarbimides are produced (Werner, *Trans.*, 1891, 59,

396). These compounds have not the properties of thiocarbamides, since they are soluble in alkalis, and are not desulphurised by mercuric oxide. They have probably the formula  $\text{NR}:\text{C}(\text{SH})\cdot\text{NR}\cdot\text{COR}$ , and this view is confirmed by the fact that the acyl derivatives of mono-substituted thiocarbamides exist in two forms, one of which behaves as a true thiocarbamide, whilst the more stable modification agrees in its properties with the ordinary acyl derivatives, which the author terms isothiocarbamides.

Acetyldiphenylisothiocarbamide,  $\text{NPh}:\text{C}(\text{SH})\cdot\text{NPhAc}$ , which has already been prepared by Deninger (Abstr., 1895, 461), melts at  $96^\circ$ , and not at  $91^\circ$  as stated by that author. Mercuric oxide converts it into the mercuric salt,  $(\text{C}_{15}\text{H}_{13}\text{ON}_2\text{S})_2\text{Hg}$ . Acetyldi-*o*-tolylisothiocarbamide, melts at  $103^\circ$ , whilst the corresponding *p*-tolyl compound melts at  $108^\circ$ . Acetyldiphenetylisothiocarbamide melts at  $98^\circ$ ; propionyldiphenylisothiocarbamide,  $\text{NPh}:\text{C}(\text{SH})\cdot\text{NPh}\cdot\text{COEt}$ , melts at  $93.5^\circ$ , whilst propionyldi-*o*-tolylisothiocarbamide melts at  $97.5^\circ$ , and the corresponding *p*-tolyl compound at  $105^\circ$ . Isovaleryldiphenylisothiocarbamide melts at  $83^\circ$ .

Acetylphenylthiocarbamide,  $\text{NHPh}\cdot\text{CS}\cdot\text{NHAc}$ , obtained by the action of acetic anhydride on phenylthiocarbamide, melts at  $139^\circ$ , but on further heating is converted into the iso-derivative melting at  $171^\circ$ . Concentrated aqueous alkalis decompose it, forming acetanilide and a thiocyanate, whilst dilute alkalis dissolve it, forming a solution from which acids precipitate the tautomeric form. It undergoes the usual reaction of a thiocarbamide with mercuric oxide, acetylphenylcarbamide being produced. The tautomeric form,  $\text{NPh}:\text{C}(\text{SH})\cdot\text{NHAc}$ , has already been described by Miquel (*Bull. Soc. Chim.*, 1875, [ii], 25, 252). Both the forms have the same molecular weight as determined by the cryoscopic method in acetic acid solution. Acetyl-*o*-tolylthiocarbamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHAc}$ , melts at  $140^\circ$  and behaves in a similar manner to the phenyl derivative. The corresponding iso-derivative has been described (Dixon, *Trans.*, 1889, 55, 304). Acetyl-*p*-tolylthiocarbamide, melts at  $137^\circ$ . Acetylphenetylthiocarbamide melts at  $137^\circ$ , and the corresponding iso-derivative at  $196^\circ$ . A. II.

[Phenylthiocarbimide] as a Reagent for the Detection of the Alcoholic Hydroxyl Group. By WILLIAM R. ORNDORFF AND F. A. RICHMOND (*Amer. Chem. J.*, 1899, 22, 458—472).—Phenylthiocarbimide combines with aliphatic monohydroxy-alcohols to form well-defined thiourethanes, but does not interact in so simple a manner with unsaturated or polyhydroxy-alcohols, phenols, aromatic alcohols, or fatty or aromatic acids. In most cases, therefore, it cannot be used as a substitute for phenylcarbimide to detect the presence of a hydroxyl group.

Ethyl phenylthiocarbamate,  $\text{NHPh}\cdot\text{CS}\cdot\text{OEt}$  or  $\text{NPh}:\text{C}(\text{SH})\cdot\text{OEt}$ , melts at  $71$ — $72^\circ$ , not at  $65^\circ$  as stated by Hofmann (*Ber.*, 1869, 2, 120; 1870, 3, 772). Methyl phenylthiocarbamate,  $\text{NHPh}\cdot\text{CS}\cdot\text{OMe}$ , or  $\text{NPh}:\text{C}(\text{SH})\cdot\text{OMe}$ , prepared like the ethyl derivative, separates from alcohol in white, triclinic crystals [ $a:b:c=0.6065:1.0:5.513$ ;  $\alpha=63^\circ 19' 57''$ ,  $\beta=128^\circ 52' 50''$ ,  $\gamma=103^\circ 8' 48''$ ], and melts at  $97^\circ$ . Propylphenylthiocarbamate,  $\text{NHPh}\cdot\text{CS}\cdot\text{OPr}^a$  or  $\text{NPh}:\text{C}(\text{SH})\cdot\text{OPr}^a$ , prepared by

heating a mixture of propyl alcohol and phenylthiocarbimide for 16 hours at  $100^{\circ}$ , crystallises from absolute alcohol in white, triclinic needles and melts at  $48^{\circ}$ ; if a higher temperature than  $100^{\circ}$  is used in the preparation, gaseous products together with thiocarbimide are formed. *Isopropyl phenylthiocarbamate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{OPr}^{\beta}$ , or  $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{OPr}^{\beta}$ , prepared similarly, separates from alcohol in brilliant, colourless, monoclinic crystals,  $[a:b:c = 0.6777:1:1.8325, \beta = 87^{\circ}28'50'']$  and melts at  $85.5^{\circ}$ . The corresponding *isobutyl* compound,

$\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\text{Pr}^{\beta}$  or  $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{O}\cdot\text{CH}_2\text{Pr}^{\beta}$ , crystallises from alcohol, and melts at  $80.5^{\circ}$ ; the *tertiary butyl* derivative,  $\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CMe}_3$ , or  $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{O}\cdot\text{CMe}_3$ , melts at the atmospheric temperature, but solidifies in a freezing mixture, forming long, white needles. *Isoamyl phenylthiocarbamate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{OC}_5\text{H}_{11}$ , or  $\text{NPh}\cdot\text{C}(\text{HS})\cdot\text{OC}_5\text{H}_{11}$ , forms white crystals and melts at about  $21^{\circ}$ .

When allyl alcohol is heated with phenylthiocarbimide, symmetrical diphenylcarbamide is formed, but no thiourethane; in like manner, glycol and glycerol give rise only to diphenylthiocarbamide (compare Tessmer, *Abstr.*, 1885, 774), whilst in the case of glycol chlorohydrin, erythritol, or dextrose no action occurs. Phenol yields thiocarbimide only, and not the corresponding thiourethane as stated by Dixon (*Trans.*, 1890, 57, 268), and Snape (*Trans.*, 1896, 69, 98); with quinol, pyrogallol, and benzyl alcohol there is no action.

On heating phenylthiocarbimide with acetic acid for 5 hours at  $100^{\circ}$ , symmetrical diphenylcarbamide is obtained; with benzoic acid under similar conditions, there is no action, whilst with lactic acid, thiocarbimide and carbimide alone are formed. W. A. D.

**Conversion of Nitrobenzene into *o*-Nitrophenol by means of Caustic Potash.** By ALFRED WOHL (*Ber.*, 1899, 32, 3486—3488).—When nitrobenzene is mixed with five times its weight of dry, finely-powdered potassium hydroxide, and the mixture heated in a closed vessel, in small quantities at a time, for 2 hours at  $60\text{--}70^{\circ}$  and then for 1 hour at  $95^{\circ}$ , 33 per cent. of the nitrobenzene is converted into *o*-nitrophenol. If the heating at  $95^{\circ}$  is omitted, about 55 per cent. of the nitrobenzene is recovered unchanged, but of the rest, 45 per cent. is converted into *o*-nitrophenol. The air is not concerned in the oxidation, for this takes place equally in a current of hydrogen. None of the ordinary products of the reduction of nitrobenzene can be detected in the product of the reaction. C. F. B.

**Reactions of Phenyl Chloroacetate.** By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 958—964).—Phenyl chloroacetate, obtained by heating together molecular proportions of phenol and chloroacetyl chloride, crystallises in colourless needles melting at  $44\text{--}45^{\circ}$  and is somewhat unstable, exposure to moist air slowly converting it into phenol and chloroacetic acid. It does not react with phenol at  $250^{\circ}$ , and is the only product of the action of chloroacetyl chloride on phenol, even at  $200^{\circ}$ ; but when heated with ethyl alcohol or sodium ethoxide, the theoretical amount of ethyl chloroacetate is formed, with liberation of phenol. The replacement of the phenoxy-group in phenyl chloroacetate is therefore effected much more readily than is

the case with phenyl chlorocarbonate (Abstr., 1899, i, 875), whilst the chlorine atom, on the other hand, possesses great stability. The action of ammonia on phenyl chloroacetate in ethereal solution results in the formation of chloroacetamide and ammonium phenoxide. The production of phenyl aminoacetate by heating phenyl chloroacetate with alcoholic ammonia at  $140^{\circ}$ , as described by Prévost (*J. pr. Chem.*, 1871, [ii], 4, 379), could not be confirmed, and the formation of such a compound seems impossible in view of the reactions described above. N. L.

**Reactions of Phenyl Chloroacetate and Phenyl Glycollate.** By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 964—969. Compare preceding abstract).—When heated with aniline (2 mols.) at  $80^{\circ}$ , phenyl chloroacetate is converted into *phenyl anilinoacetate*,  $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Ph}$ , which crystallises in small, colourless scales melting at  $82\text{--}83^{\circ}$ , and is soluble in alcohol, ether, chloroform, benzene, or strong acids; boiling with alcohol converts it into ethyl anilinoacetate, with liberation of phenol. If, however, phenyl chloroacetate is boiled with aniline, anilinoacetoanilide is formed. Phenyl chloroacetate reacts with phenylhydrazine at  $50^{\circ}$  to form *phenyl phenylhydrazinoacetate*,  $\text{N}_2\text{H}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{Ph}$ , which crystallises in small, colourless scales melting at  $93\text{--}94^{\circ}$ . Pyridine slowly enters into combination with phenyl chloroacetate and yields a yellowish-white, unstable compound,  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Ph}\cdot\text{C}_5\text{NH}_5$ , which is readily decomposed by water. Sodium phenoxide is without action on phenyl chloroacetate in the cold, but on heating a good yield of *phenyl phenoxyacetate* is obtained; this crystallises in slender, colourless, monoclinic needles melting at  $58^{\circ}$ , and is converted by boiling with alcohol into the corresponding ethyl ester, with liberation of phenol. When treated with ammonia in ethereal solution, it yields phenoxyacetamide, whilst boiling with aniline converts it into phenoxyacetanilide. Excess of ammonia or of aniline at  $200^{\circ}$  has no action on the second phenoxy-group, and in this respect phenyl phenoxyacetate differs greatly from diphenyl carbonate. From these results, it appears that chloroacetyl chloride, phenyl chloroacetate, and phenyl phenoxyacetate, on the one hand, and carbonyl chloride, phenyl chlorocarbonate, and diphenyl carbonate, on the other, belong to two distinct classes, the first being derived from a substance of complex function, whilst the second includes derivatives of a symmetrical compound. N. L.

**Action of Chlorodinitrobenzene on Potassium Benzoate and on Acetamide.** By OTTO KUM (*Ber.*, 1899, 32, 3539—3540).—Dinitrophenyl benzoate (Abstr., 1899, i, 647) is produced when potassium benzoate is heated with chlorodinitrobenzene at  $180^{\circ}$ , although no action occurs in a boiling alcoholic solution. Similarly, chlorodinitrobenzene and acetamide do not interact in alcoholic solution, but when heated together at  $200\text{--}210^{\circ}$  give dinitroaniline; in presence of sodium acetate, dinitrophenol is produced. T. M. L.

**Ethers of Isonitrosoguaiacol in their Relation to the Space Isomerism of Nitrogen.** By JOHN L. BRIDGE and W. CONGER MORGAN (*Amer. Chem. J.*, 1899, 22, 484—488).—The authors have

repeated the work of Pfob (Abstr., 1898, i, 71) and of Rupe (*ibid.*, i, 72) in the hope of isolating stereoisomeric forms of the ethers of isonitrosoguaiacol analogous with the stereoisomeric ethers of toluquinone-*m*-oxime (Abstr., 1899, i, 130, and this vol., i, 103); such space-isomerides do not, however, appear to exist.

The *benzoyl* derivative,  $C_{14}H_{11}O_4N$ , of isonitrosoguaiacol crystallises from alcohol in straw-coloured, dendritic crystals, and when heated begins to decompose at  $175^\circ$ , and melts at  $185$ – $188^\circ$ ; the *dibromide*,  $C_{14}H_{11}O_4NBr_2$ , is a yellowish-white substance which melts and decomposes at  $153$ – $154^\circ$ , and cannot be purified by crystallisation owing to decomposition occurring.

*Bromoisonitrosoguaiacol*,  $C_{14}H_{10}O_4NBr$ , prepared by boiling the dibromide with alcohol, crystallises from the latter in well-defined prisms and melts and decomposes at  $178^\circ$ .  
W. A. D.

**Relation between the Structure of Metaphenol [*m*-Hydroxybenzyl] Haloids and their Behaviour towards Alkalis.** By KARL AUWERS (*Ber.*, 1899, 32, 3583–3587).—The compounds  $OH \cdot C_6Br_3H \cdot CH_2X$  ( $X = Cl, Br, I$ ) [ $CH_2X : OH : Br_3 = 1 : 3 : 2 : 4 : 6$ ],  $OH \cdot C_6Br_4 \cdot CH_2Br$  [ $= 3 : 2 : 4 : 5 : 6 : 1$ ];  $OH \cdot C_6Br_3(CH_2X) \cdot CH_2 \cdot OR$  ( $X = Br, I$ ;  $R = H, Me, Et, Ac$ ) [ $= 4 : 3 : 5 : 6 : 2 : 1$ ];  $OH \cdot C_6Br_3(CH_2Br)_2$  [ $= 5 : 2 : 4 : 6 : 1 : 3$ ];  $OH \cdot C_6Br_3(CH_2Br) \cdot CH_2 \cdot OMe$  [ $= 2 : 3 : 5 : 6 : 4 : 1$ ];  $OH \cdot C_6Br_2(CH_2 \cdot OR)_2 \cdot CH_2Br$  ( $R = H, Me$ ) [ $= 5 : 3 : 6 : 2 : 4 : 1$ ];  $OH \cdot C_6Br_3(CHBr_2) \cdot CH : Y$  [ $Y = O, (OMe)_2, (OEt)_2, (OAc)_2$ ] [ $= 5 : 3 : 4 : 6 : 1 : 2$ ] all dissolve in cold dilute aqueous sodium hydroxide without appreciably decomposing after 15 minutes; but the compounds  $OH \cdot C_6MeBr_3Z \cdot CH_2Br$  ( $Z = Br, CH_2 \cdot OMe$ ) [ $= 2 : 1 : 3 : 6 : 5 : 4$ ];  $OH \cdot C_6MeBr_3 \cdot CH_2Br$  [ $= 4 : 1 : 3 : 5 : 6 : 2$ ];  $OH \cdot C_6Me_3Br \cdot CH_2Br$  [ $= 5 : 2 : 4 : 6 : 1$ ];  $OH \cdot C_6Me_2Br_2 \cdot CH_2X$  ( $X = Cl, Br, I$ ) [ $= 5 : 2 : 4 : 3 : 6 : 1$ ] decompose almost instantaneously under these conditions with loss of the halogen of the  $CH_2X$  group. It thus appears that the presence of a methyl group in the nucleus of a *m*-phenol haloid renders the latter very sensitive to the action of alkalis, although if a hydrogen atom of the methyl group is replaced by a negative radicle, such as  $OH$ ,  $OMe$ ,  $OEt$ , or  $OAc$ , this influence is no longer exercised; those *m*-phenol haloids which contain two methyl groups are much more rapidly decomposed than those containing only one.  
W. A. D.

**Degradation of Phenols during Bromination.** By KARL AUWERS and O. ANSELMINO (*Ber.*, 1899, 32, 3587–3597).—Although homologues of phenol yield normal substitution derivatives when heated with bromine in sealed tubes, they yield bromo-derivatives of the next lower homologue when treated with bromine in an open vessel, the methyl group in the *p*-position relative to the hydroxyl being replaced by a bromine atom; in no case, however, has the replacement of an ortho- or meta-methyl group been observed. The alkyl ethers and acetyl derivatives of phenols behave towards bromine in like manner. It appears that the elimination of a methyl group under the conditions cited depends on atmospheric moisture, since when this is excluded normal substitution occurs; by adding a small quantity of water or aqueous hydrobromic acid, the displacement of a methyl radicle is greatly accelerated.

When dibromo- $\psi$ -cumenol or dibromo- $p$ -hydroxy- $\psi$ -cumyl bromide is left in contact with an excess of bromine for 4 hours at the ordinary temperature, it is converted into tribromo- $p$ -xylenol [ $\text{OH} : \text{Me}_2 = 1 : 2 : 5$ ]. When  $\psi$ -cumenol tribromide (m.p.  $128^\circ$ ) is treated similarly, it gives rise after  $1\frac{1}{2}$  hours to the compound  $\text{CH}_2\text{Br} \cdot \text{C} \begin{smallmatrix} \nwarrow \text{C}(\text{CH}_2\text{Br}) : \text{CBr} \\ \swarrow \text{CBr} \text{---} \text{CMe} \end{smallmatrix} \cdot \text{C} \cdot \text{OH}$  (this vol., i, 162), but after 5 hours 2 : 5 : 6-tribromo-3-hydroxy- $p$ -xylyl bromide alone is obtained; this crystallises from light petroleum in slender, lustrous needles, melts at  $118\text{--}119^\circ$ , yields tribromo- $p$ -xylenol (m. p.  $178\text{--}179^\circ$ ) on reduction with zinc dust and acetic acid, and is converted by the further action of bromine into an intractable resin.

Pentabromo- $\psi$ -cumenol [ $\text{OH} : \text{Br}_2 : (\text{CH}_2\text{Br})_3 = 5 : 3 : 6 : 1 : 2 : 4$ ] is stable towards bromine at the ordinary temperature, but at  $100^\circ$ , in presence of a small quantity of aqueous hydrobromic acid, yields tribromo- $p$ -xylylene bromide,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \nwarrow \text{CBr} : \text{C}(\text{CH}_2\text{Br}) \\ \swarrow \text{C}(\text{CH}_2\text{Br}) : \text{CBr} \end{smallmatrix} \text{CBr}$ , which crystallises from glacial acetic acid in small, white, silky needles ( $+ \text{C}_2\text{H}_4\text{O}_2$ ), which slowly effloresce and then melt at  $184^\circ$ ; it is insoluble in aqueous alkalis, and yields an *acetyl* derivative,  $\text{C}_{10}\text{H}_7\text{O}_2\text{Br}_5$ , which crystallises from glacial acetic acid in asbestos-like fibres and melts at  $162^\circ$ .

Tribromo- $o$ -xylenol [ $\text{Me}_2 : \text{OH} = 1 : 2 : 4$ ], when left with bromine at the ordinary temperature, gives rise after 3 hours to tetrabromo- $m$ -cresol; the tetrabromide,  $\text{OH} \cdot \text{C}_6\text{Br}_3\text{Me} \cdot \text{CH}_2\text{Br}$  [ $\text{Me} : \text{CH}_2\text{Br} : \text{OH} = 1 : 2 : 4$ ], and the pentabromide,  $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2$  [ $(\text{CH}_2\text{Br})_2 : \text{OH} = 1 : 2 : 4$ ], derived from  $o$ -xylenol yield, on being warmed with bromine for an hour, tetrabromo- $m$ -hydroxybenzyl bromide (this vol., i, 162). Tribromo- $m$ -xylenol [ $\text{Me}_2 : \text{OH} = 1 : 3 : 4$ ] probably gives rise initially to the bromide  $\text{OH} \cdot \text{C}_6\text{MeBr}_3 \cdot \text{CH}_2\text{Br}$  [ $\text{Me} : \text{CH}_2\text{Br} : \text{OH} = 1 : 2 : 4$ ], but subsequently yields tetrabromo- $o$ -cresol (Bodroux, Abstr., 1898, i, 641), which can also be obtained by heating  $o$ -cresol with bromine during 4 hours at  $100^\circ$ . Tribromo- $p$ -hydroxy- $m$ -xylylene bromide [ $(\text{CH}_2\text{Br})_2 : \text{OH} = 1 : 3 : 4$ ] is stable towards bromine at the ordinary temperature, but on digesting for several hours at  $100^\circ$  with an excess of bromine containing aqueous hydrobromic acid, yields tetrabromo- $o$ -hydroxybenzyl bromide, which is also obtained by heating  $o$ -cresol with bromine for 8 hours at  $100^\circ$ ; this crystallises from glacial acetic acid or light petroleum in needles and melts at  $158\text{--}159^\circ$ .

Tetrabromo- $p$ -cresol is readily converted by bromine into pentabromophenol, the acetate of which crystallises from glacial acetic acid in lustrous needles and melts at  $196\text{--}197^\circ$ ; whilst 3 : 5-dibromo-4-hydroxybenzyl bromide (Auwers and Daecke, this vol., i, 164) yields a mixture of tribromo- and tetrabromo-phenol. W. A. D.

**Action of Chloroform and Alkali on 1 : 3 : 4-Xylenol.** By KARL AUWERS (*Ber.*, 1899, 32, 3598—3599).—Reimer's reaction gives abnormal results with 1 : 3 : 4-xylenol as with  $\psi$ -cumenol (Abstr., 1885, 380; 1886, 143; 1896, i, 420); in addition to 2-hydroxy-4 : 5-dimethylbenzaldehyde, which crystallises from dilute alcohol in long needles or thin plates and melts at  $40\text{--}42^\circ$ , there is formed a considerable quantity of the compound  $\text{C}_9\text{H}_{10}\text{OCl}_2$ , which crystallises from light petroleum, melts at  $102\text{--}103^\circ$ , and is derived from the aldehyde by the replace-

ment of an oxygen atom by two atoms of chlorine, although being insoluble in alkalis, its structure is uncertain. W. A. D.

**Oxidation Products of Phenols and Bromophenols and the Constitution of the Isomeric Tribromo- $\psi$ -cumenol.** By KARL AUWERS (*Ber.*, 1899, 32, 3440—3453).—A theoretical discussion of the compounds described in the following three abstracts.

R. H. P.

**Oxidation Product of Pseudocumenol Tribromide** [Tribromo- $\psi$ -cumenol]. By KARL AUWERS and A. EBNER (*Ber.*, 1899, 32, 3454—3465).—On treating tribromo- $\psi$ -cumenol with a mixture of nitric and acetic acids, an oxy-compound,  $\text{CO} \begin{smallmatrix} \text{CBr} \cdot \text{CMe} \\ \text{CMe} \cdot \text{CBr} \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2\text{Br}$ ,

is obtained, which crystallises in compact prisms melting at  $158^\circ$ , on reduction yields dibromo- $\psi$ -cumenol, and by acetic anhydride is converted into the diacetate of dibromo- $p$ -hydroxy- $\psi$ -cumyl alcohol. The corresponding *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2\text{O} \cdot \text{CH}_2\text{Br}$ , obtained by treatment with acetyl chloride, forms compact, white crystals melting at  $118$ — $119^\circ$ . On treating the oxy-compound dissolved in methyl alcohol

with caustic soda and acidifying, an *oxide*,  $\text{CO} \begin{smallmatrix} \text{CBr} \cdot \text{CMe} \\ \text{CMe} \cdot \text{CBr} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{CH}_2 \end{smallmatrix}$ ,

is precipitated; it crystallises in long needles melting at  $109$ — $110.5^\circ$ , and with acetyl bromide yields an isomeric *acetyl* derivative,  $\text{C}_6\text{Me}_2\text{Br}_2\text{O} \cdot \text{CH}_2 \cdot \text{OAc}$ , which crystallises in white leaflets melting at  $103^\circ$ . The *diacetate*,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OAc}$ , obtained by treating the acetyl derivative (m. p.  $119^\circ$ ) with zinc dust and acetic acid, or the acetyl derivative (m. p.  $103^\circ$ ) with sodium acetate and acetic acid, forms white leaflets melting at  $95^\circ$ . With acetyl chloride, the oxide forms an *additive* compound,  $\text{C}_6\text{Me}_2\text{Br}_2\text{ClO} \cdot \text{CH}_2 \cdot \text{OAc}$ , which crystallises in small needles melting at  $96$ — $98^\circ$ .

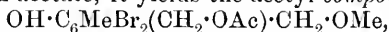
The *monomethyl ether* of dibromo- $p$ -hydroxy- $\psi$ -cumylene *o*-glycol,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \parallel \\ \text{CMe} \cdot \text{CBr} \cdot \text{C} \end{smallmatrix} \text{CH}_2 \cdot \text{OMe}$ , obtained by treating the oxy-compound

with methyl alcohol and sodium hydroxide, forms small needles melting at  $149^\circ$ ; the corresponding *monoethyl ether* melts at  $113$ — $114^\circ$ . The *diacetate* of the methyl ether is obtained by the action of acetic anhydride, and forms yellowish prisms melting at  $107$ — $108^\circ$ .

**3:6-Dibromo-5-hydroxy- $\psi$ -cumylene dibromide**,  $\text{OH} \cdot \text{C}_6\text{MeBr}_2(\text{CH}_2\text{Br})_2$ , prepared by the action of hydrogen bromide on the methyl ether just described, forms compact, short needles melting at  $151$ — $152^\circ$ , and is insoluble in alkalis. The *acetyl* derivative forms lustrous needles melting at  $132$ — $133^\circ$ . If a concentrated solution of the dibromide in methyl alcohol is left for some time, the portion which can be precipitated by water is soluble in alkalis, and is the *methyl ether* of 3:6-dibromo-5-hydroxy- $\psi$ -cumylene bromohydrin,  $\text{OH} \cdot \text{C}_6\text{MeBr}_2(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OMe}$ , which forms short needles melting at  $107$ — $108^\circ$ ; on reduction, it yields the *methyl ether*,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , melting at  $92^\circ$ .

By the continued action of methyl alcohol on the dibromide, 3:6-dibromo-5-hydroxy- $\psi$ -cumylene *dimethyl ether* is obtained, crystallising in compact prisms melting at  $79$ — $80^\circ$ ; it is converted by the action

of dry hydrogen chloride into the *methyl* ether of the chlorohydrin,  $\text{OH}\cdot\text{C}_6\text{MeBr}_2(\text{CH}_2\text{Cl})\cdot\text{CH}_2\cdot\text{OMe}$ , which melts at  $93-95.5^\circ$ ; on treatment with sodium acetate, it yields the *acetyl compound*,



which forms white leaflets melting at  $110-111^\circ$ .

R. H. P.

**Dibromo-*m*-hydroxy- $\psi$ -cumyl Bromide.** By KARL AUWERS and TH. MAAS (*Ber.*, 1899, 32, 3466—3475. Compare *Abstr.*, 1898, i, 343).—

3 : 6-Dibromo-5-hydroxy- $\psi$ -cumyl bromide,  $\text{CMe}\begin{smallmatrix} \text{C(OH)}\cdot\text{CBr} \\ \text{CBr}=\text{CMe} \end{smallmatrix}\text{C}\cdot\text{CH}_2\text{Br}$ ,

prepared by treating the diacetate of 3 : 6-dibromo-5-hydroxy- $\psi$ -cumyl alcohol with hydrogen bromide, crystallises in long, silky needles melting at  $128^\circ$ , and forms an *acetyl* derivative melting at  $105-106^\circ$ . On boiling with alcohol, it yields the *ethyl* ether of 3 : 6-dibromo-5-hydroxy- $\psi$ -cumyl alcohol melting at  $63-64^\circ$ . The *acetyl* derivative of the corresponding methyl derivative melts at  $80-81^\circ$ . The diacetate first mentioned, on reduction with sodium amalgam, yields the *diacetate* of 3-bromo-5-hydroxy- $\psi$ -cumyl alcohol, which forms colourless prisms melting at  $65^\circ$ . The *monoacetate*, obtained when the reduction is effected with zinc dust and acetic acid, crystallises in small needles melting at  $104^\circ$ . Both acetates, on hydrolysis, yield the 3-bromo-5-hydroxy- $\psi$ -cumyl alcohol, which forms lustrous, white leaflets melting at  $164^\circ$ . 5-Hydroxy- $\psi$ -cumyl alcohol, prepared by the reduction of 3 : 6-dibromo-5-hydroxy- $\psi$ -cumyl alcohol with sodium amalgam, crystallises in lustrous leaflets melting at  $153^\circ$ , and with bromine yields 6-bromo-5-hydroxy- $\psi$ -cumyl bromide, which forms long needles melting at  $116^\circ$ , and with sodium acetate yields the *acetyl* derivative of the corresponding alcohol melting at  $103^\circ$ . R. H. P.

**Oxidation Products of Phenols and Bromophenols.** By KARL AUWERS and J. BROICHER [and in part W. WOLFF] (*Ber.*, 1899, 32, 3475—3486. Compare preceding abstracts and *Abstr.*, 1898, i, 30).—

The *acetyl* derivative,  $\text{CO}\begin{smallmatrix} \text{CMe}\cdot\text{CBr} \\ \text{CMe}\cdot\text{CBr} \end{smallmatrix}\text{CMe}\cdot\text{OAc}$ , obtained by treat-

ing the oxy-compound of dibromomesitol with acetic anhydride, forms rhombohedra melting at  $94-95^\circ$ . The oxy-compound of 3 : 5 : 6-tribromo-1 : 2 : 4-xylenol forms a *monoacetate* melting at  $116-117^\circ$ , and a *diacetate* melting at  $101-102^\circ$ , which, on treatment with hydrogen bromide, yields  $\omega : 2 : 5 : 6$ -tetrabromo-1 : 3 : 4-xylenol, melting at  $138-139^\circ$  and forming an *acetyl* derivative which melts at  $110-111^\circ$ . The constitution of the tetrabromo-compound is proved by its preparation in several stages from  $\omega\omega : 3 : 5 : 6$ -pentabromo-1 : 2 : 4-xylenol.

the *methyl* ether,  $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CBr}\cdot\text{CBr} \\ \text{CBr}\cdot\text{CBr} \end{smallmatrix}\text{C}\cdot\text{CH}_2\cdot\text{OMe}$ , melting at  $176-178^\circ$  being obtained as an intermediate product.

$\omega : 2 : 4 : 5 : 6$ -Pentabromocresol, obtained by the action of bromine on the tetrabromo-compound, forms silky needles melting at  $136-137^\circ$ .

The following derivatives of tribromomesitol were prepared in a similar manner to those of tribromo- $\psi$ -cumenol (see preceding abstracts).

An oxy-compound,  $\text{CO}\begin{smallmatrix} \text{CMe}\cdot\text{CBr} \\ \text{CMe}\cdot\text{CBr} \end{smallmatrix}\text{C(OH)}\cdot\text{CH}_2\text{Br}$ , which crystallises



in prisms melting at 145—146° and forms an *acetyl* derivative melting at 126—127°, and the corresponding *oxide*, which forms compact needles, melting at 118—119°.

$\omega\omega$ :3:5:6-Pentabromo-1:2:4-xenol yields an *oxy*-compound which crystallises in lustrous, monoclinic prisms melting at 188—190° and forms an *acetyl* derivative melting at 145—146°. R. H. P.

**Preparation of Aromatic Thiols.** By EDOUARD BOURGEOIS (*Rec. Trav. Chim.*, 1899, 18, 426—450).—The author describes improvements in the working of the two methods used for the preparation of aromatic thiols: the reduction of aromatic sulphochlorides, and the hydrolysis of aromatic derivatives of xanthogenic acid.

Phenyl mercaptan, prepared by the first method, has no alliaceous odour and boils at 169·5° under 760 mm. pressure.

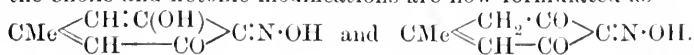
*p*-Tolyl mercaptan boils at 195° under 760 mm. pressure (Vallin gave 194°).

$\beta$ -Naphthyl mercaptan boils under the ordinary pressure at 288° with partial decomposition into di- $\beta$ -naphthyl sulphide and hydrogen sulphide; it is slightly volatile in steam, not non-volatile as stated in Beilstein.

*m*-Tolyl mercaptan boils at 195·4° under 760 mm. pressure and has a specific gravity 1·06251 at 0°/4°. T. H. P.

**Constitution of Mononitrosoresorcinol.** By FERDINAND HENRICH (*Ber.*, 1899, 32, 3419—3424. Compare Abstr., 1897, i, 446).—Nitrosoresorcinol is the oxime of an orthoquinone, and not of a paraquinone as has been previously assumed; the aminophenol formed on reducing the monomethyl ether of nitrosoresorcinol readily gives an *acetyl* derivative,  $\text{NHAc}\cdot\text{C}_6\text{H}_2\text{Me}(\text{OMe})\cdot\text{OH}$ , which crystallises from dilute alcohol in needles and melts at 156—157°; when this is heated, it undergoes ortho-condensation and gives *methoxy- $\mu$ -methyltoluoxazole*,  $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Me}\langle\text{O}\rangle\text{CMe}$ , which crystallises from alcohol, melts at 71·5—72°, and when heated under pressure with concentrated hydrochloric acid gives aminoresorcinol hydrochloride, methyl chloride, and acetic acid. This view is confirmed by a comparison of the monomethyl ether of nitrosoresorcinol with Kietaihl's two nitroso-derivatives from resorcinol monomethyl ether (Abstr., 1899, i, 343), since it closely resembles the ortho-derivative in physical and chemical properties; a green *labile modification* of the latter has been obtained which passes sharply into the stable yellow modification when heated to 120°.

Of the two possible formulæ for nitrosoresorcinol, the diortho-formula is preferred, since substitution takes place most readily in this position, and the enolic and ketonic modifications are now formulated as



T. M. L.

**Action of Methylene Sulphate on Benzyl Alcohol.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1899, [iii], 21, 1059—1061).—The action of methylene sulphate on benzyl alcohol at 60—65° results

in the formation of dibenzylformal and benzyl hydrogen sulphate. *Dibenzylformal*,  $\text{CH}_2(\cdot\text{O}\cdot\text{CH}_2\text{Ph})_2$ , is a colourless liquid of faint benzylic odour, boils at about  $330^\circ$  and does not solidify at  $-23^\circ$ ; it is resinified by concentrated sulphuric acid, and is converted into benzyl iodide by the action of fuming hydriodic acid. *Benzyl hydrogen sulphate* itself could not be prepared in the pure state, since its aqueous solution becomes resinified on evaporation. The *barium* salt,  $\text{Ba}(\text{SO}_4\cdot\text{CH}_2\text{Ph})_2 + 2\text{H}_2\text{O}$ , crystallises from water in long, colourless needles; the anhydrous salt, obtained by cooling a solution in 80 per cent. alcohol, slowly resinifies on keeping and decomposes when heated even below  $80^\circ$ ; its aqueous solution deposits barium sulphate when concentrated by heat. The *potassium* salt crystallises from alcohol in anhydrous, slender needles which are stable below  $100^\circ$ . The *silver* and *lead* salts undergo decomposition when their aqueous solutions are concentrated, but the greenish *copper* salt, which crystallises with  $4\text{H}_2\text{O}$ , is more stable.

N. L.

**Action of Bromine on *p*-Hydroxybenzyl Alcohol.** By KARL AUWERS and S. DAECKE (*Ber.*, 1899, 32, 3373—3381. Compare following abstract).—*p*-Hydroxybenzyl alcohol is best prepared by Hutchinson's method (*Abstr.*, 1891, 561) and crystallises from water in large, colourless prisms or compact needles melting at  $124.5\text{--}125.5^\circ$  and not at  $110^\circ$  as stated by Biedermann (*Abstr.*, 1887, 38) and Hutchinson.

3:5-Dibromo-4-hydroxybenzyl bromide,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$ , obtained by the action of an acetic acid solution of bromine on a solution of the hydroxy-alcohol in the same solvent, crystallises from light petroleum in small, colourless needles melting at  $149\text{--}150^\circ$ ; it dissolves readily in cold ether, also in warm benzene or acetic acid, but is insoluble in alkalis. Its constitution follows from the fact that when reduced it yields Werner's dibromo-*p*-cresol (*Bull. Soc. Chim.*, 1886, [ii], 46, 278). The *acetyl* derivative,  $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$ , crystallises from light petroleum in large crystals melting at  $76.5\text{--}77.5^\circ$  and is only sparingly soluble in cold methyl or ethyl alcohol. When the tribromide is shaken with acetone and water, it is converted into 3:5-dibromo-4-hydroxybenzyl alcohol,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OH}$ , which crystallises from benzene in compact, colourless plates melting at  $116\text{--}117^\circ$ , and is readily soluble in ether or alcohol. The corresponding ethers,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OR}$ , are obtained when the tribromide is heated with the requisite alcohol. The *methyl* ether crystallises in glistening needles melting at  $71\text{--}72^\circ$ , and the *ethyl* ether in small prisms melting at  $93.5\text{--}94.5^\circ$ . The *acetate*,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OAc}$ , obtained by the action of an acetic acid solution of anhydrous sodium acetate on the tribromide, crystallises from light petroleum in compact prisms melting at  $114.5\text{--}115.5^\circ$ ; it dissolves in alkalis, but rapidly undergoes decomposition when the alkali is too strong; it is also decomposed when boiled with different alcohols, yielding the corresponding ethers. The isomeric *acetate*,  $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OH}$ , is obtained when a solution of the acetyl derivative of 3:5-dibromo-4-hydroxybenzyl iodide in acetone is treated with moist silver oxide for several days at the ordinary temperature, and forms a yellowish oil. The *diacetate*,

$\text{OAc} \cdot \text{C}_6\text{H}_4\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OAc}$ , crystallises in prisms melting at  $68-70^\circ$ ; it may be obtained by the action of acetic anhydride on the hydroxybenzyl alcohol or on either of the monoacetyl derivatives, and when its acetic acid solution is treated with hydrogen iodide at  $80^\circ$  it yields 3:5-dibromo-4-hydroxybenzyl iodide, which crystallises from benzene in yellow needles melting at  $148-149^\circ$ ; when hydrogen iodide is employed at the ordinary temperature, the product is the *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{H}_4\text{Br}_2 \cdot \text{CH}_2\text{I}$ , which crystallises in colourless needles melting at  $94-95^\circ$ . J. J. S.

**Action of Bromine on *m*-Hydroxybenzyl Alcohol.** By KARL AUWERS and W. RICHTER (*Ber.*, 1899, 32, 3381—3384. Compare *Abstr.*, 1897, i, 335, 336, and preceding abstract).—When a warm acetic acid solution of *m*-hydroxybenzyl alcohol, which is best obtained by von den Velden's method (*Journ.*, 1877, ii, 338), is treated with bromine also dissolved in acetic acid, 2:4:6-tribromo-3-hydroxybenzyl bromide,  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2\text{Br}$ , is formed; it crystallises in small needles melting at  $149^\circ$ , and dissolves readily in alkalis, and in most organic solvents except light petroleum. On reduction with zinc dust and acetic acid, it yields Claus and Hirsch's tribromo-*m*-cresol melting at  $84^\circ$  (*Abstr.*, 1889, 389). Its *acetyl* derivative crystallises in glistening needles and melts at  $104^\circ$ .

*Tribromohydroxybenzyl acetate*,  $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$ , forms small needles melting at  $133^\circ$ ; when hydrolysed with alcoholic sodium hydroxide, it yields 2:4:6-tribromo-3-hydroxybenzyl alcohol, melting at  $130^\circ$ ; this is not readily converted into its ethers by the action of different alcohols.

The *diacetate*,  $\text{OAc} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$ , crystallises from a mixture of ether and light petroleum in small prisms melting at  $83-84^\circ$ .

2:4:6-Tribromo-3-hydroxybenzyl chloride, obtained by the action of dry hydrogen chloride on a hot acetic acid solution of the alcohol, crystallises in needles melting at  $133^\circ$ , and the *iodide*, obtained by shaking an alcoholic solution of the bromide with a concentrated aqueous solution of potassium iodide, crystallises in glistening, feathery needles melting at  $146^\circ$ . J. J. S.

**Tribromo-derivatives of  $\psi$ -Cumenol and Mesitol.** By KARL AUWERS, F. A. TRAUN, and R. WELDE (*Ber.*, 1899, 32, 3297—3309. Compare this vol., i, 96; and *Abstr.*, 1897, i, 34 and 335; 1898, i, 646; 1899, i, 343).—The *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , prepared from 3:6-dibromo-4-hydroxy- $\psi$ -cumyl methyl ether, crystallises from light petroleum or glacial acetic acid in white needles, melts at  $114-114.5^\circ$ , and is not acted on by gaseous hydrogen chloride in boiling acetic acid solution; at  $150^\circ$ , or in presence of zinc chloride at  $100^\circ$ , hydrogen chloride converts the acetate into the chloride,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{Cl}$ , which melts at  $110^\circ$ , and yields an *acetyl* derivative crystallising in white needles and melting at  $150-150.5^\circ$ . Hydrogen bromide converts the *acetyl* derivative melting at  $114-114.5^\circ$  into *dibromo-p-acetoxy- $\psi$ -cumyl bromide*,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{Br}$ , which melts at  $161^\circ$ , and on reduction with zinc dust and acetic acid yields the *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{Me}_3\text{Br}_2$ , melting at  $80.5-81^\circ$ , derived from

dibromo-*p*- $\psi$ -cumenol; hydrogen iodide behaves similarly, giving rise to *dibromo-p-acetoxy- $\psi$ -cumyl iodide*,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{I}$ , which crystallises from glacial acetic acid in felted needles, melts at  $174\text{--}175^\circ$ , and can also be obtained by the action of hydrogen iodide on the diacetate melting at  $105\text{--}106^\circ$ , derived from dibromo-*p*-hydroxy- $\psi$ -cumyl alcohol. The iodide is converted by moist silver oxide into the corresponding alcohol,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , which melts at  $122\text{--}122.5^\circ$  (Auwers and Sheldon, Abstr., 1898, i, 647); this is not acted on by boiling alcohol or aqueous acetone, but is hydrolysed by alcoholic potash to dibromo-*p*-hydroxy- $\psi$ -cumyl alcohol (m. p.  $166^\circ$ ).

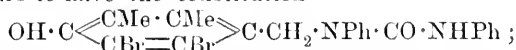
The isomeric acetate,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CBr} \cdot \text{CMe} \\ \text{CMe} \cdot \text{CBr} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{OAc}$  (m. p.  $114^\circ$ ), which is prepared by the action of sodium acetate on  $\psi$ -cumenol bromide and is insoluble in alkalis, is, on the other hand, hydrolysed instantaneously by alcohol or aqueous acetone. When dibromo-*p*-acetoxy- $\psi$ -cumyl iodide is heated with silver oxide in benzene solution, it is converted into the ether,  $(\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2)_2\text{O}$  (Auwers and Avery, Abstr., 1896, i, 150). 2:6-Dibromo-4-hydroxymesityl methyl ether,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , prepared by heating mesitol tribromide with methyl alcohol, crystallises in thick, monoclinic plates, and melts at  $142^\circ$ ; the *acetyl* derivative crystallises from dilute acetic acid in small plates, melts at  $109\text{--}110^\circ$ , and is converted by hydrogen iodide into 2:6-dibromo-4-acetoxymesityl iodide,  $\text{OAc} \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{CH}_2\text{I}$ , which separates from glacial acetic acid or acetone in slender, silky needles, and melts at  $176\text{--}177^\circ$ . 2:6-Dibromo-4-acetoxymesityl alcohol,  $\text{OAc} \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , prepared by decomposing the iodide with aqueous acetone, crystallises from light petroleum in felted needles, melts at  $128^\circ$ , and is converted by alcoholic potash into 2:6-dibromo-4-hydroxymesityl alcohol (m. p.  $186^\circ$ ); with acetic anhydride, it yields the diacetate (m. p.  $159\text{--}160^\circ$ ), whilst hydrogen bromide converts it into 2:6-dibromo-4-acetoxymesityl bromide,  $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{Br}$  (m. p.  $150\text{--}151^\circ$ ).

In the light of these results, the structure of the acetyl derivatives obtained by the action of sodium acetate on phenol bromides which are insoluble in aqueous alkali is discussed; these must be regarded as similar in structure to the corresponding phenol bromides, and therefore, like the latter, can be represented by three formulæ (compare this vol., i, 96) which cannot as yet be differentiated.

The phenylurethane,  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , formed by the action of phenylcarbimide on mesitol tribromide (compare Auwers and Allendorff, Abstr., 1899, i, 32), melts and decomposes at  $257^\circ$ ,\* and on reduction with zinc dust and acetic acid is converted into the *phenylurethane*,  $\text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , of dibromomesitol, which can also be prepared from the latter by the action of phenylcarbimide; this cannot be obtained in well-defined crystals, and melts somewhat indefinitely between  $213^\circ$  and  $216^\circ$ . When the phenylurethane of mesitol tribromide, dissolved in xylene, is heated with aniline (2 mols.), it yields the *phenylurethane*,  $\text{NHPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , of 2:6-dibromo-4-hydroxymesitylaniline, which forms short, slender

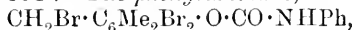
\* ?  $227^\circ$ , compare Auwers and Allendorff, *loc. cit.*, who give  $226^\circ$ , and p. 3300 of original.—W. A. D.

needles, melts at 190—194°, and is easily hydrolysed by alcoholic potassium hydroxide to dibromo-*p*-hydroxymesitylaniline (m. p. 136°). The latter substance, when treated with phenylcarbimide, gives rise to a *phenylurethane* which readily dissolves in aqueous alkalis, is isomeric, not identical, with the phenylurethane melting at 190—194°, and hence appears to have the constitution



the phenylcarbimide, in fact has attacked the anilino- in preference to the hydroxyl group, and with *p*-aminophenol a similar behaviour is observed, *p*-hydroxydiphenylcarbamide,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , being formed; this crystallises from dilute alcohol in lustrous, pearl-grey needles, melts at 216—217°, and is easily soluble in aqueous alkalis. The use of phenylcarbimide as a means of recognising the presence of a hydroxyl group in organic compounds must therefore be limited to compounds which do not contain an amino-radicle.

The *phenylurethane*,  $\text{OAc} \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , obtained by the action of phenylcarbimide on dibromo-*p*-hydroxymesityl acetate (m. p. 165—166°), prepared from mesitol tribromide and sodium acetate, crystallises from glacial acetic acid in short, slender needles and melts at 163—164°. The *phenylurethane*,



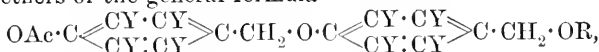
can be obtained only with difficulty from dibromo-*p*-hydroxy- $\psi$ -cumyl bromide, and separates from hot glacial acetic acid as a white powder melting at 225—230°.

W. A. D.

**Dibromo-*p*-hydroxymesityl Alcohol.** By KARL AUWERS and F. A. TRAUN (*Ber.*, 1899, 32, 3309—3317).—4:6-Dibromo-2-amino-*m*-xylene, prepared by reducing the corresponding nitro-compound, crystallises from 75 per cent. alcohol in slender, felted needles, melts at 99—100°, and is converted by the diazo-reaction into 4:6-dibromo-2-hydroxy-*m*-xylene, which crystallises from light petroleum in slender needles and melts at 132—133°; the *acetate* of the latter separates from alcohol or glacial acetic acid in white leaflets and melts at 79—80°. 2:6-Dibromo-4-hydroxymesityl alcohol,  $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , prepared from the foregoing hydroxy-compound by the Lederer-Manasse reaction, using formaldehyde and dilute aqueous sodium hydroxide, crystallises from xylene, melts at 186°, and is identical with the compound melting at 191—192° formed by acting with aqueous acetone on mesitol tribromide (the bromide of dibromoanhydro-*p*-hydroxymesityl alcohol, Auwers and Allendorff, *Abstr.*, 1899, i, 32). When the hydroxy-alcohol is heated for several hours at 160—170°, it is converted into *tetrabromo- $p$ -dihydroxydimesityl ether*,  $(\text{OH} \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{CH}_2)_2\text{O}$ , which is nearly insoluble in all the ordinary solvents, melts at 256°, and is identical with the compound formerly stated (Auwers and Allendorff, *loc. cit.*) to be isomeric with the hydroxy-alcohol; the latter conclusion was arrived at because preparations melting at 252°, on being heated with benzene or xylene, appeared to be converted into the hydroxy-alcohol melting at 192°. It is now shown, however, that the impure hydroxy-alcohol, containing small quantities of the ether, when heated, undergoes conversion into the

latter, and melts at  $252^{\circ}$ , although the pure hydroxy-alcohol, when similarly treated, remains unchanged and melts at  $192^{\circ}$ . The samples formerly heated with benzene or xylene and supposed to consist of the compound melting at  $252^{\circ}$ , in reality consisted mostly of the hydroxy-alcohol, and the apparent regeneration of the latter is thus explained. The diacetate of the ether melts at  $229^{\circ}$  and is identical with the compound prepared by the action of silver oxide on the acetyl derivative of dibromo-*p*-hydroxymesityl bromide (*loc. cit.*); by digestion with methyl iodide and sodium methoxide, the ether yields the *dimethyl* derivative,  $O(C_6Me_2Br_2 \cdot OMe)_2$ , which crystallises from a mixture of absolute alcohol and benzene in slender, white needles and melts at  $205-206^{\circ}$ . W. A. D.

**Substituted Phenyl Benzyl Ethers.** By KARL AUWERS, F. A. TRAUN, and R. WELDE (*Ber.*, 1899, 32, 3317—3331).—By the action of sodium alkyl oxides on acetylated hydroxybenzyl haloids of the type  $OAc \cdot C \begin{smallmatrix} \swarrow CY \cdot CY \\ \searrow CY : CY \end{smallmatrix} C \cdot CH_2X$ , where X represents a halogen and Y any substituent, crystalline compounds are obtained, which the author formerly regarded as stilbene derivatives of the type  $OAc \cdot C \begin{smallmatrix} \swarrow CY \cdot CY \\ \searrow CY : CY \end{smallmatrix} C \cdot CH : CH \cdot C \begin{smallmatrix} \swarrow CY \cdot CY \\ \searrow CY : CY \end{smallmatrix} C \cdot OAc$  (*Annalen*, 1898, 301, 260), but are shown in the present paper to be substituted phenylbenzyl ethers of the general formula



R denoting the alkyl radicle.

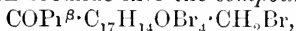
The *ether*,  $OAc \cdot C_6Me_2Br_2 \cdot CH_2 \cdot O \cdot C_6Me_2Br_2 \cdot CH_2 \cdot OEt$ , prepared by the action of alcoholic sodium ethoxide on dibromo-*p*-acetoxy- $\psi$ -cumyl bromide, melts at  $175-176^{\circ}$ , and has been already described as tetrabromodiacetoxytetramethylstilbene (Auwers and Sheldon, *Annalen*, 1898, 301, 272); the corresponding *ether*,  $C_{22}H_{24}O_4Br_4$ , prepared from dibromo-*p*-acetoxy-mesityl bromide (Auwers and Allendorff, *Abstr.*, 1899, i, 32) melts at  $217-218^{\circ}$ . The former of these is converted by gaseous hydrogen bromide in glacial acetic acid solution at  $80^{\circ}$  into the *ether*,  $OAc \cdot C_{17}H_{14}OBr_4 \cdot CH_2Br$ , which crystallises from glacial acetic acid or xylene in needles and melts at  $219-221^{\circ}$ ; at  $100^{\circ}$ , or more rapidly at the boiling point of acetic acid,  $\psi$ -cumenol tribromide (m. p.  $126^{\circ}$ ) is formed. The isomeric mesitol derivative, melting at  $217-218^{\circ}$ , gives rise under similar conditions to the *ether*  $C_{20}H_{19}O_3Br_5$ , which crystallises from xylene in needles and melts at  $254-255^{\circ}$ . The *ether*,  $OAc \cdot C_{17}H_{14}OBr_4 \cdot CH_2I$ , prepared by the action of hydrogen iodide on the  $\psi$ -cumyl derivative melting at  $175-176^{\circ}$  melts and decomposes at  $219-221^{\circ}$ , and cannot be crystallised from xylene or benzene without decomposition occurring; at  $100^{\circ}$ , hydrogen iodide gives rise to dibromo-*p*-hydroxy- $\psi$ -cumyl iodide, although hydrogen chloride, under similar conditions, is without action, and only begins to act at  $150^{\circ}$ , when dibromo-*p*-hydroxy- $\psi$ -cumyl chloride is formed.

The *methyl ether*,  $OAc \cdot C_{17}H_{14}OBr_4 \cdot CH_2 \cdot OMe$ , prepared by the action of sodium methoxide on dibromo-*p*-acetoxy- $\psi$ -cumyl bromide, crystallises from glacial acetic acid in slender needles and melts at  $202-204^{\circ}$ ,

whilst the isomeric *mesityl* derivative crystallises similarly, melts at  $220-221^{\circ}$ , and can also be obtained by the interaction of dibromo-*p*-hydroxymesityl methyl ether with sodium methoxide and dibromo-*p*-acetoxymesitylbromide. The latter fact shows that the action of sodium alkyl oxides on acetylated hydroxybenzyl haloids takes place in two stages. Hydrogen bromide converts the mesityl derivative, melting at  $220-221^{\circ}$ , into the bromide,  $\text{OAc}\cdot\text{C}_{17}\text{H}_{11}\text{OBr}_4\cdot\text{CH}_2\text{Br}$ , already described.

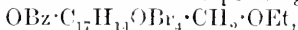
The *amyl ether*,  $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\cdot\text{OC}_5\text{H}_{11}$ , crystallises from glacial acetic acid in slender needles and melts at  $146-147^{\circ}$ ; the isomeric *mesityl* compound has similar properties, and melts at  $163-164^{\circ}$ . Hydrogen bromide interacts with these substances in the same manner as with the analogous ethyl and methyl ethers.

By the action of sodium ethoxide on dibromo-*p*-isobutyroxy- $\psi$ -cumyl bromide (*Annalen*, 1898, 301, 280), small quantities of *dibromo-p-isobutyroxy- $\psi$ -cumyl ethyl ether*,  $\text{COPr}^{\beta}\cdot\text{O}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OEt}$ , melting at  $74-75^{\circ}$ , are formed, together with a larger proportion of the *ether*,  $\text{COPr}^{\beta}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\cdot\text{OEt}$ , which crystallises from alcohol in white needles and melts at  $147-148^{\circ}$ ; the *mesityl* derivative isomeric with the latter crystallises from glacial acetic acid in silky needles and melts at  $182-183^{\circ}$ . The  $\psi$ -cumyl ether (m. p.  $147-148^{\circ}$ ) is converted by hydrogen bromide into the compound



which forms slender needles and melts at  $192-193^{\circ}$ ; the isomeric *mesityl* derivative melts at  $221-223^{\circ}$ , but was not obtained pure.

The *benzoyl* derivative,  $\text{OBz}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$ , of dibromo-*p*-hydroxymesityl bromide crystallises from glacial acetic acid or petroleum in long, lustrous needles, melts at  $160-161^{\circ}$ , and is converted by sodium ethoxide into the corresponding *ether*,



which crystallises from benzene or glacial acetic acid in white, felted needles, melts at  $222-223^{\circ}$ , and when treated with hydrogen bromide gives rise to the corresponding *bromide*,  $\text{C}_{25}\text{H}_{21}\text{O}_3\text{Br}_5$ , which crystallises from xylene in white needles and melts at  $234-235^{\circ}$ .

*Dibromo-p-acetoxy- $\psi$ -cumyl dibromo-p- $\psi$ -cumyl ether*,



prepared by reducing the corresponding bromide (m. p.  $219-221^{\circ}$ ) with zinc dust and acetic acid, crystallises from glacial acetic acid in white, felted needles, melts at  $204-205^{\circ}$ , and on digestion with sodium methoxide yields dibromo- $\psi$ -cumenol, methyl acetate, and dibromo-*p*-hydroxy- $\psi$ -cumyl methyl ether; when treated with hydrogen bromide in hot glacial acetic acid solution, the ether gives rise to a mixture of dibromo- $\psi$ -cumenol and dibromo-*p*-hydroxy- $\psi$ -cumyl bromide.

When the bromide,  $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\text{Br}$ , is boiled with sodium acetate and glacial acetic acid or acetic anhydride, the corresponding *acetate*,  $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\cdot\text{OAc}$ , melting at  $204-205^{\circ}$  is formed; but if acetic anhydride is employed and the time of heating increased, large quantities of the diacetyl derivative (m. p.  $105-106^{\circ}$ ) of dibromo-*p*-hydroxy- $\psi$ -cumyl alcohol are obtained.

W. A. D.

**Hydrolysis of Benzonitrile.** By CHARLES RABAUT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1075—1076).—If 10 grams of benzonitrile are dissolved in 100 c.c. of alcohol and heated in a reflux apparatus for an hour with 6 grams of potassium hydroxide, 98 per cent. of the theoretical amount of benzamide is produced, but if only 1.12 or 0.56 gram of potassium hydroxide is used, the yield is reduced to 70 or 40 per cent. respectively. With concentrated potash, the product consists almost entirely of benzoic acid. No benzamide is formed when a dilute alcoholic solution of benzonitrile is heated for an hour in a sealed tube at 100°.

N. L.

**Isomeric Change of *o*-Amino- and *o*-Nitro-cinnamonitriles.** By ROBERT PSCHORR and O. WOLFES (*Ber.*, 1899, 32, 3399—3405. Compare Abstr., 1899, i, 491).— *$\alpha$ -p-Methoxyphenyl-*o*-nitrocinnamonitrile*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , crystallises from toluene or alcohol in minute, felted, yellow needles, melts at 162° (corr.), and sublimes without decomposition. *2-Amino-3- $p$ -methoxyphenylquinoline*,  $\text{NH}_2 \cdot \text{C}_9\text{NH}_5 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , prepared by reducing the preceding compound with tin and hydrochloric acid, crystallises from alcohol in colourless needles and melts at 151—152° (corr.); the salts are only slightly soluble, the *nitrate* melts at 207° (corr.), the *hydrochloride* at 226° (corr.), and the sulphate at 228° (corr.); the *platinichloride* forms yellow needles and decomposes at 240° (corr.), and the *picrate* forms minute, yellow needles and melts at 256° (corr.). *3- $p$ -Methoxyphenyl-2-carbostyryl*,  $\text{OH} \cdot \text{C}_9\text{NH}_5 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , prepared by the action of nitrous acid on the amino-compound, or by the action of acetic anhydride and sulphuric acid on  *$\alpha$ -paramethoxyphenyl-*o*-aminocinnamic acid*, crystallises from alcohol in minute, colourless needles and melts at 259° (corr.).

Frost's  *$\alpha$ -phenyl-*o*-nitrocinnamonitrile* (Abstr., 1889, 597), on reduction, gives *2-amino-3-phenylquinoline* (Pschorr, Abstr., 1899, i, 491).

*$\alpha$ - $p$ -Nitrophenyl-*o*-acetaminocinnamonitrile* can be converted directly by alcoholic hydrochloric acid into *2-amino-3- $p$ -nitrophenylquinoline*.

By heating with potassium hydroxide in dilute alcoholic solution,  *$\alpha$ -phenyl-*o*-nitrocinnamic nitrile* is converted into hydrogen cyanide and *benzoylanthranilic acid*, which can also be prepared by the action of benzoyl chloride on anthranilic acid; it crystallises from alcohol in minute, colourless needles, melts at 181° (corr.), and gives a *monomethyl ester*, which crystallises from alcohol in colourless needles and melts at 101.5°. Similarly,  *$\alpha$ - $p$ -methoxyphenyl-*o*-nitrocinnamic nitrile* is converted by alcoholic potash into *anisoylanthranilic acid*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , which crystallises from alcohol in scales and melts at 232° (corr.).

T. M. L.

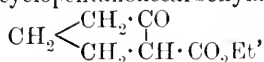
**Tautomerism of *o*-Benzoylbenzoic Acid.** By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1899, 129, 1213—1216).—The formation of diphenylphthalide from *o*-benzoylbenzoic chloride points to the existence of a tautomeric form,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CPhCl} \\ \text{CO} \end{smallmatrix} \text{O}$ , for this com-



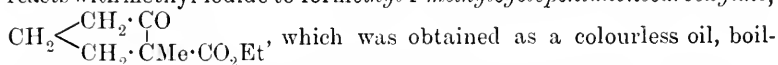
pound. With a view of ascertaining whether methyl esters corresponding with the two forms of the acid are capable of existence, its esterification was carried out by five different methods. The *methyl* ester crystallising in colourless prisms and melting at 52° was obtained in every case.

G. T. M.

**Synthesis of Cyclopentane Derivatives by means of Ethyl Adipate.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1019—1023).—Ethyl 2-cyclopentanonecarboxylate,



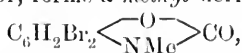
was shown by Dieckmann (*Abstr.*, 1894, i, 173) to be formed by the action of sodium on ethyl adipate at 120°, and by a modification of the original process the author has obtained this compound in the pure state as a colourless, oily liquid, boiling at 113° under 22 mm. pressure, and having a sp. gr. 1.0976 at 0°. The sodium and potassium salts crystallise well and are not decomposed by water; the copper salt crystallises in thin, green plates melting at 183°, and dissolves in chloroform, yielding a violet solution. The *phenylhydrazone* is an oily liquid, whilst the *semicarbazone* crystallises in large, white needles melting at 143°. The sodium derivative of ethyl 2-cyclopentanonecarboxylate reacts with methyl iodide to form *methyl 1-methylcyclopentanonecarboxylate*,



which was obtained as a colourless oil, boiling at 108° under 22 mm. pressure, and having a sp. gr. 1.0529 at 0°. This forms a white, crystalline *semicarbazone* melting at 153°, and differs from its lower homologue in being insoluble in alkalis. When heated with concentrated hydrochloric acid, it yields 1-methylcyclopentanone, which Montemartini obtained by heating calcium adipate; this boils at 139°, and has a sp. gr. 0.7379 at 0°. It forms a liquid *oxime*, which boils at 103° under 22 mm. pressure, and yields a crystalline *benzoyl* derivative melting at 63.5°, and a crystalline *semicarbazone* which melts at 184° (Montemartini gives 171°). When boiled with alcoholic potash, ethyl methylcyclopentanonecarboxylate yields the potassium salt of  $\alpha$ -methyladipic acid; if, however, a large excess of alkali is not employed, the potassium ethyl salt,  $\text{CO}_2\text{K} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , is formed, which resists further hydrolysis.

N. L.

**Action of Potassium Hypobromite on Amides of Hydroxybenzoic Acids.** By W. VAN DAM (*Rec. Trav. Chim.*, 1899, 18, 408—425).—By the action of potassium hypobromite on salicylamide, two dibromocarboxylaminophenols are obtained, one melting at above 270° and the other at 255° (McCoy, *Abstr.*, 1899, i, 359, gave the melting point 250°), which is not identical with the compound obtained by Jacoby by the direct bromination of carboxylaminophenol; Jacoby's compound is found to melt at 255°, not at 243° as stated by him. The dibromocarboxylaminophenol melting at 255°, obtained by McCoy and by the author, forms a *methyl* derivative,



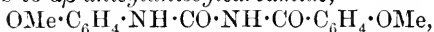
melting at 124°, an *acetyl* derivative,  $\text{C}_6\text{H}_2\text{Br}_2 \begin{array}{c} \text{O} \\ \text{NAc} \end{array} \text{CO}$ , and a

barium compound,  $\text{C}_6\text{H}_2\text{Br}_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{Nba} \end{smallmatrix} \text{CO}$ , crystallising in white needles; it is readily soluble in acetone or alcohol, less so in ether or water, and from its solution in caustic potash solution the *potassium* derivative,  $\text{C}_6\text{H}_2\text{Br}_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{NK} \end{smallmatrix} \text{CO}$ , is deposited in white needles. Jacoby's compound does not form salts.

By the action of potassium hypobromite on *m*-hydroxybenzamide, *s*-tribromo-*m*-hydroxybenzamide  $[\text{CONH}_2 : \text{OH} : \text{Br}_3 = 1 : 3 : 2 : 4 : 6]$  melting at  $221^\circ$  is obtained; if excess of alkali is present, tribromo-*m*-aminophenol melting at  $117^\circ$  is formed, the *triacetyl* compound of which,  $\text{OAc} \cdot \text{C}_6\text{HBr}_3 \cdot \text{NAc}_2$ , melts at  $136^\circ$ .

The action of barium hypobromite on *p*-hydroxybenzamide gives rise to dibromo-*p*-aminophenol melting at  $191^\circ$ .

Under the influence of bromine and sodium methoxide, anisoyl-amide condenses to  $\alpha\beta$ -anisylanisoylcarbamide,



which melts at  $222^\circ$ .

The intramolecular change produced in the bromamides by the action of an alkali, by which they are converted into amides, is shown to be a reaction of the first order. T. H. P.

**Anisonitrile.** By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 466—467).—*p*-Methoxybenzonitrile and *p*-ethoxybenzonitrile described by Reinders and Ringer (*Abstr.*, 1899, i, 893) have already been prepared (Henry, *Ber.*, 1870, 2, 667; Pinner, *Abstr.*, 1891, 63).

T. H. P.

**Resolution of Racemic Amino-acids into Optically Active Components.** By EMIL FISCHER (*Ber.*, 1899, 32, 3638—3646. Compare *Abstr.*, 1899, i, 888).—A good yield of racemic benzoyl-tyrosine is obtained from *p*-hydroxy- $\alpha$ -benzoylaminocinnamic acid by a modification of Erlenmeyer and Halsey's method (*Abstr.*, 1898, i, 197). This compound is resolved into its active components by fractional crystallisation from aqueous solutions of its alkaloidal salts.

When brucine is employed, the first crop of crystals consists of the corresponding salt of benzoyl-*l*-tyrosine. Benzoyl-*l*-tyrosine crystallises in leaflets and melts at  $165$ — $166^\circ$ , this temperature being  $30^\circ$  lower than the melting point of the racemic compound;  $[\alpha]_D$  in an 8 per cent. alkaline solution at  $20^\circ$  is  $19.25^\circ$ , and with a 5 per cent. solution is  $18.29^\circ$ . *l*-Tyrosine is prepared by hydrolysing the benzoyl derivative with 10 per cent. hydrochloric acid; a more concentrated acid produces racemisation. The specific rotation in 20 per cent. hydrochloric acid at  $20^\circ$  is  $-8.64^\circ$ , corresponding with the value  $-8.48^\circ$  obtained by Schultze and Bosshard for the natural product; in 4 per cent. acid  $[\alpha]_D$  is greater, that of the synthesised compound being  $-13.2^\circ$ , whilst that of a specimen obtained from casein is  $-12.56^\circ$ ; the latter result, however, does not agree with that of the above investigators, who found the rotation to be  $-15.6^\circ$ .

Natural tyrosine, when rapidly heated, melts at  $310$ — $312^\circ$ , whilst the racemic compound melts about  $2^\circ$  higher; the former separates in long, flexible crystals, the latter crystallises in stout needles,

*Benzoyl-d-tyrosine* is obtained from the racemic compound by the aid of cinchonine. The alkaloid salt separates somewhat slowly in flattened needles, and is obtained pure after two crystallisations. The *benzoyl* derivative melts at  $165.5^{\circ}$ ; in an alkaline solution  $[\alpha]_D$  is  $-19.59^{\circ}$ .

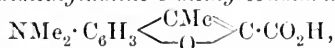
*d-Tyrosine*, dissolved in 21 per cent. hydrochloric acid, has  $[\alpha]_D$   $8.64^{\circ}$ . A base, supposed to be *d*-tyrosine, has been isolated by von Lippmann from the white shoots of the sugar beet in 25 per cent. hydrochloric acid; it gave  $[\alpha]_D$   $6.85^{\circ}$ .

The mother liquor from the brucine salt of *benzoyl-l-tyrosine* contains a mixture of racemic and dextro-salts; these are converted into the corresponding tyrosines, which are treated with hydrochloric acid, when the hydrochloride of the racemic base crystallises first; the *d*-tyrosine obtained from the mother liquor has a higher specific rotation than that obtained from the cinchonine salt. G. T. M.

**Coumarins. I. Behaviour of Aminophenols with Ethyl Acetoacetate.** By HANS VON PECHMANN (*Ber.*, 1899, 32, 3681—3690).—A summary and a discussion of previous results and of those enumerated in the following three abstracts. It is only *m*-aminophenols which condense with ethyl acetoacetate. R. H. P.

**Coumarins. II. 7-Dimethylamino-4-methylcoumarin and Homologues.** By HANS VON PECHMANN and MAX SCHAAL (*Ber.*, 1899, 32, 3690—3696).—*p*-Dimethylaminophenol and ethyl acetoacetate condense in the presence of zinc chloride to form 7-dimethylamino-4-methylcoumarin, which crystallises from dilute alcohol, with  $3H_2O$ , in the form of yellowish needles melting at  $143^{\circ}$ . On fusion with alkalis, it yields traces of 2-hydroxy-4-dimethylaminoacetophenone, which forms white leaflets melting at  $120^{\circ}$ , and a compound melting at  $142^{\circ}$ , which is probably bis-dimethylaminodihydrocoumarone,  $C_{16}O_2H_{10}Me_2(NMe_2)_2$ . Nitrous or nitric acid converts the 7-dimethylamino-4-methylcoumarin into a mononitro-derivative melting at  $159^{\circ}$  and a dinitro-derivative melting at  $230^{\circ}$ . Bromine in chloroform

solution yields the dibromide,  $NMe_2 \cdot C_6H_3 \begin{smallmatrix} \diagup CMeBr \cdot CHBr \\ \diagdown O \end{smallmatrix}$ , which crystallises from glacial acetic acid in white needles melting and decomposing at  $210^{\circ}$ , and on boiling with alcohol is converted into 3-bromo-7-dimethylamino-4-methylcoumarin melting at  $169^{\circ}$ . On treatment of this monobromo-derivative with bromine, two isomeric dibromo-derivatives are obtained, one melting at  $126^{\circ}$ , the other at  $184^{\circ}$ . On dissolving the dibromide or the monobromo-derivative in alcoholic potash, 6-dimethylamino-3-methylcoumarilic acid,



is obtained; it forms grey needles melting and decomposing at  $165^{\circ}$ , and on heating yields 6-dimethylamino-3-methylcoumarone, which melts at  $58^{\circ}$ .

*m*-Dimethylaminophenol, ethyl acetoacetate, and alcohol condense in the presence of zinc chloride to form 7-dimethylamino-4-methyl-3-ethylcoumarin, which when crystallised from alcohol melts at  $89^{\circ}$ , but from benzene and light petroleum at  $135^{\circ}$ .

*7-Diethylamino-4-methylcoumarin*, obtained when *m*-diethylamino-phenol is used, is an oil which yields a *tribromo*-derivative melting at 109°. R. H. P.

**Coumarins. III. 7-Amino-4-Methylcoumarin.** By HANS VON PECHMANN AND OTTO SCHWARZ (*Ber.*, 1899, 32, 3696—3699).—*7-Amino-4-methylcoumarin*, prepared by the condensation of *m*-aminophenol and ethyl acetoacetate with zinc chloride, crystallises in fern-shaped forms, which sinter at 215° and melt at about 223°; it yields a *monoacetyl* derivative melting at 270°, and a *monobenzoyl* derivative melting at 249—250°. *7-Methylamino-4-methylcoumarin*, obtained in a similar manner from *m*-methylaminophenol, crystallises from dilute alcohol, with H<sub>2</sub>O, in the form of small, yellow needles melting at 123°, and yields a *nitrosamine* melting at 189°. On heating *7-amino-4-methylcoumarin* with methyl iodide in a sealed tube at 100°, *4-methylcoumarin-7-trimethylammonium iodide*,  $\text{NMe}_3\text{I} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} < \text{CMe} \cdot \text{CH} \\ \text{O} - \text{CO} \end{smallmatrix}$ , is

obtained; it forms needles melting at 188°, and yields an insoluble *platinichloride*. The position of the amino-group in these coumarins is proved by the conversion of the aminocoumarin into *4-methylumbelliferone*. R. H. P.

**Coumarins. IV. Action of *m*-Aminophenol on Ethyl Acetoacetate.** By HANS VON PECHMANN AND OTTO SCHWARZ (*Ber.*, 1899, 32, 3699—3704).—In the condensation of *m*-aminophenol with ethyl acetoacetate by means of zinc chloride, in addition to *7-amino-4-methylcoumarin*, varying proportions of *7* (?) *-hydroxylepidone* (Besthorn and Byvanek, *Abstr.*, 1898, i, 450), *7* (?) *-hydroxy-2:4:4-trimethyl-3:4-dihydroquinoline*, and *4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin* are formed.

*7-Hydroxylepidone* forms a *monoacetyl* derivative melting at 250—254°, and a *monobenzoyl* derivative melting at 288°.

*7* (?) *-Hydroxy-2:4:4-trimethyl-3:4-dihydroquinoline* can be prepared by heating together molecular proportions of *m*-aminophenol and *mesityl oxide*; it forms a grey, amorphous powder without a definite melting point, and on treatment with ethyl acetoacetate and an alcoholic solution of zinc chloride yields *4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin*, which forms yellow needles melting at 268°, and on treatment with bromine yields *5* (?) *:10-dibromo-4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin dibromide*; this is obtained in the form of greenish-yellow needles which melt and decompose at 204°, and on treatment with alcoholic potash give *3:5* (?) *:10-tribromo-4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin*, which forms small, yellow needles melting and decomposing at 191°. Either of the bromine compounds on continued boiling with alcoholic potash gives *4* (?) *:9-dibromo-3:5:5:7-tetramethyl-5:6-dihydrodibromocoumarilic acid*, which melts and decomposes at 206°, and yields a *methyl ester* melting at 138°.

Molecular proportions of *m*-aminophenol and ethyl acetoacetate, when heated on the water-bath for 3 hours, give *ethyl m-hydroxyphenylaminocrotonate*,  $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ , which at a temperature of 250—260° yields *4:7* (?) *-dihydroxy-2-methylquinoline*; this

crystallises, with  $\text{H}_2\text{O}$ , in the form of needles, which decompose at  $300^\circ$  without melting, and forms a *diacetyl* derivative melting at about  $232^\circ$ .  
R. H. P.

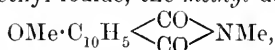
**Derivatives of Naphthalic Acid.** By FRITZ ANSELM and F. ZUCKMAYER (*Ber.*, 1899, **32**, 3283—3296).—Concentrated sulphuric acid does not act on naphthalic acid ( $1:8$ -naphthalenedicarboxylic acid) at a high temperature, but sulphuric acid containing 25 per cent. of anhydride gives rise at  $90$ — $95^\circ$  to the *monosulphonic* derivative,  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_5(\text{CO}_2\text{H})_2$ , a white, deliquescent substance which melts at  $198^\circ$ , being converted into the anhydride; the *barium* and *calcium* salts (each with  $1\text{H}_2\text{O}$ ) and the *sodium* and *potassium* salts (each with  $1\frac{1}{2}\text{H}_2\text{O}$ ) were prepared.

On adding nitric acid (1 mol.) to naphthalic anhydride dissolved in sulphuric acid at  $5^\circ$ , the *mononitro*-derivative,  $\text{NO}_2\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$ , is obtained; it crystallises from glacial acetic acid in slightly brownish, lustrous leaflets and melts at  $249^\circ$  (compare Quincke, *Abstr.*, 1888, 843). On nitration with a mixture of sulphuric acid and 2 mols. of fuming nitric acid at  $60^\circ$ , naphthalic anhydride yields the *dinitro*-derivative,  $\text{C}_{10}\text{H}_4(\text{NO}_2)_2(\text{CO})_2\text{O}$ , which crystallises from toluene in yellowish-brown needles and melts at  $214^\circ$ . *Aminonaphthalic anhydride*, prepared by reducing the corresponding nitro-compound, is a yellow powder which melts above  $300^\circ$  and is nearly insoluble in all solvents, but the *acetyl* derivative,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$ , crystallises from glacial acetic acid in yellowish-white needles; *diaminonaphthalic anhydride* was obtained only in the form of the *tin* salt. The *calcium* salt,  $\text{Ca}[\text{SO}_3\cdot\text{C}_{10}\text{H}_4(\text{NO}_2)(\text{CO}_2)_2\text{Ca}]_2$ , of nitrosulphonaphthalic acid, obtained by nitrating sulphonaphthalic acid, forms stout, yellow crystals.

*Hydroxynaphthalic anhydride*,  $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$ , prepared by heating sodium sulphonaphthalate with solid potassium hydroxide initially at  $180^\circ$ , finally at  $220^\circ$ , crystallises from glacial acetic acid in bright yellow, silky needles ( $+\frac{1}{3}\text{C}_2\text{H}_4\text{O}_2$ ), which on drying lose the acetic acid and become lustreless; the anhydride dissolves in alkalis to form initially a yellow salt by replacement of the hydroxylic hydrogen by the metal, but this immediately changes into a normal, colourless salt, owing to fission of the anhydride ring; the *potassium* salt,  $\text{C}_{12}\text{H}_6\text{O}_5\text{K}_2$ , forms beautiful, white needles. Since the hydroxy-anhydride unites with diazo-salts to form dyes, it appears probable that the hydroxyl group is not in the ortho- but in the para-position relatively to carboxyl; the hydroxy-anhydride can also be obtained from aminonaphthalic anhydride through the diazo-reaction. Like phthalic anhydride, hydroxynaphthalic anhydride furnishes cherry-red dyes of the naphthalein and rhodamine types. *Acetoxynaphthalic anhydride*,  $\text{OAc}\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$ , prepared by heating the hydroxy-anhydride with acetic anhydride, crystallises from ethyl acetate in white leaf-

lets, and melts at  $216^\circ$ . *Hydroxynaphthalimide*,  $\text{OH}\cdot\text{C}_{10}\text{H}_5\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{smallmatrix}\text{NH}$ , prepared by heating the anhydride with alcoholic ammonia, crystallises from dilute acetic acid in yellowish-green needles, and shows no definite melting point; the *acetyl* derivative,  $\text{C}_{14}\text{H}_9\text{O}_4\text{N}$ , forms white

leaflets and melts at 278°. On heating the potassium salt of hydroxynaphthalimide with methyl iodide, the *methyl* derivative,

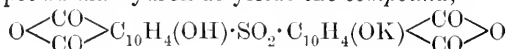


is formed, which separates from alcohol in yellowish-white, crystalline masses. *Hydroxynaphthalanilide*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{NPh}$ , prepared by heating the anhydride with aniline for 4 hours at 185°, crystallises from alcohol in yellowish-white, felted needles and melts above 300°; the *acetyl* derivative,  $\text{OAc} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{NPh}$ , forms white needles and melts at 212°.

*Hydroxynaphthaloxime*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{N} \cdot \text{OH}) \end{array} \text{O}$ , prepared by heating hydroxynaphthalic anhydride with alcoholic hydroxylamine hydrochloride and sodium acetate, crystallises from alcohol in lemon-yellow, sheaf-like aggregates of needles, and has no definite melting point; it yields intensely red salts with alkalis; the *potassium* salt,  $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{N} \cdot \text{OK}) \end{array} \text{O}$ , forms beautiful needles. *Diacetoxynaphthaloxime*,  $\text{OAc} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{N} \cdot \text{OAc}) \end{array} \text{O}$ , crystallises from alcohol in long, colourless needles and melts at 194°. On heating the potassium salt of the oxime with methyl iodide for 5 hours at 100°, the *dimethyl ether*,  $\text{OMe} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{N} \cdot \text{OMe}) \end{array} \text{O}$ , is obtained; it crystallises from alcohol in white, felted needles and melts at 191°. The *phenylhydrazone*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{N} \cdot \text{NHPh}) \end{array} \text{O}$ , forms dark yellow needles and melts at 265°.

*Methoxynaphthalic anhydride*, prepared by heating the hydroxynaphthalic anhydride with methyl iodide and sodium methoxide, crystallises from ethyl acetate in yellowish-white needles and melts at 244°.

*Hydroxysulphonaphthalic anhydride*, prepared by the action of fuming sulphuric acid (25 per cent.  $\text{SO}_3$ ) on hydroxynaphthalic anhydride at 115–120°, crystallises from water on adding alcohol in slightly yellow sheaves of needles; the *sodium* salt crystallises similarly, and on fusion with potassium hydroxide yields the compound,



or  $\text{O} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_{10}\text{H}_4(\text{SO}_3\text{K}) \cdot \text{O} \cdot \text{C}_{10}\text{H}_4(\text{OH}) \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$ , which forms yellow crystals and is insoluble in most solvents. W. A. D.

**Methyl Phloroglucinolcarboxylate.** By JOSEF HERZIG and FRANZ WENZEL (*Ber.*, 1899, 32, 3541–3542. Compare Will and Albrecht, *Abstr.*, 1884, 1335).—*Methyl phloroglucinolcarboxylate*,  $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CO}_2\text{Me}$ , is readily obtained by the action of methyl iodide on the silver salt of the acid in the absence of any solvent. It crystallises from aqueous methyl alcohol in short, white needles melting at 166–168°, and is readily soluble in ether, alcohol, or

ethylic acetate. The *ethyl* ester may be obtained by a similar process, but does not crystallise readily. J. J. S.

**Preparation of Hydroxystyrogallol.** By FRANZ SLAMA (*Chem. Centr.*, 1899, ii, 967; from *Diss. Giessen.*, 1899, 29—34).—By the condensation of *p*-coumaric acid with gallic acid, *hydroxystyrogallol* or 2 : 3 : 6-*trihydroxyanthracoumarin*,  $C_{16}H_8O_6$ , is formed. The properties of this substance resemble those of Jacobsen and Julius' (Abstr., 1888, 56) and of Kostanecki's (Abstr., 1888, 291) compound. The more hydroxyl groups contained in the compound, the higher is the melting point, the more intense the colour, and the less the solubility. Hydroxystyrogallol is less soluble than styrogallol. The former dissolves in sulphuric acid, forming a red, and in potassium hydroxide or ammonia forming a green, solution. *Triacetoxystyrogallol*,  $C_{16}H_5O_6(OAc)_3$ , melts at about  $250^\circ$  in a vacuum.

E. W. W.

**Solanthic Acid.** By W. BRÄUTIGAM (*Chem. Centr.*, 1899, ii, 669; from *Pharm. Zeit.*, 44, 638).—*Solanthic acid*,  $C_9H_{10}O_{10}$ , prepared from the flowers and stems of *Helianthus annuus*, crystallises from water, melts at  $144^\circ$ , sublimes without decomposition, is soluble in alcohol, ether, or water, and forms crystalline salts. The acid is probably contained in the plant in the form of the calcium salt. E. W. W.

**Metallic Derivatives of Salicylhydramide.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1899, [iii], 21, 943—945).—*Cupric methylsalicylimide*,  $Cu(O \cdot C_6H_4 \cdot CH : NMe)_2$ , obtained from the action of salicylaldehyde on cupric acetate and methylamine in alcoholic solution, or by adding a concentrated aqueous solution of cupric acetate to an alcoholic solution of methylsalicylimide, crystallises in long, dark green needles melting at  $157^\circ$ . *Cupric benzylsalicylimide*,  $Cu(O \cdot C_6H_4 \cdot CH : N \cdot CH_2Ph)_2$ , obtained in a similar manner from benzylsalicylimide, is an olive-green, crystalline substance which melts at  $204^\circ$ . A crystalline salt, having most probably the composition  $Cu[O \cdot C_6H_4 \cdot CH(NMe_2)_2]_2$ , is also yielded by dimethylamine.

The formation of these compounds leads the author to conclude that the compounds which Ettling (*Annalen*, 1840, 35, 241) obtained by the action of salicylhydramide on ammoniacal solutions of cupric acetate and ferric tartrate, are to be considered as derivatives of salicylimide of the type  $Cu(O \cdot C_6H_4 \cdot CH : NR)_2$ , and not as compounds of cuprammonium and ferrammonium respectively. N. L.

**Preparation of Anisaldehyde.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1076—1077).—A yield of about 70 per cent. of anisaldehyde is obtained by the following modification of Cannizaro's original method. 1 part of anethole is mixed with 2 parts of anhydrous acetic acid and the liquid warmed, at first gently, and then more strongly, with  $3\frac{1}{2}$  parts of nitric acid of  $14^\circ$  B. The insoluble oil which separates, together with a further portion which is obtained by saturating the aqueous liquid with sodium carbonate, is agitated with sodium hydrogen sulphite and the resulting crystalline mass

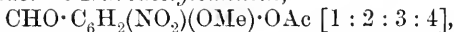
drained, washed with alcohol and ether, and treated in the usual manner. N. L.

**Aldehyde-Musk.** By ALBERT BAUR-THURGAU and AUGUST BISCHLER (*Ber.*, 1899, 32, 3647—3648. Compare Abstr., 1898, i, 523).—Butylxylylaldehyde is best prepared by heating the corresponding glyoxylic acid with *p*-toluidine and treating the product with sulphuric acid; it crystallises in large tablets melting at 60° and readily yields an *oxime*, which forms white plates melting at 97—98°. Nitric acid of 95 per cent. converts the aldehyde into a *mononitro*-compound, which crystallises in yellow, odourless plates melting at 66°. Nitric acid of 100 per cent., on the other hand, yields the *dinitro*-compound,  $C_{13}H_{16}O_5N_2$  (aldehyde-musk, German Patent, No. 94019), crystallising in faintly yellow tablets melting at 112°. It yields two *oximes* of the same composition,  $C_{13}H_{17}O_5N_3$ ; the one more readily soluble in alcohol is a microcrystalline powder melting at 138—139°, whilst the second *oxime* forms white plates melting at 171°. Aldehyde-musk readily forms condensation products with various compounds; the derivative,  $C_{14}H_{17}O_6N_3$ , obtained from nitromethane melts at 206°.

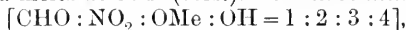
Acetic anhydride converts aldehyde-musk into a *diacetyl* derivative,  $C_{17}H_{26}O_6N_2$ , melting at 147°, which can also be obtained by converting butylxylylaldehyde into the *diacetyl* derivative melting at 87°, and treating this with nitric acid.

In the preparation of the aldehyde from butylxylylglyoxylic acid, a second compound is obtained, which has the composition  $C_{26}H_{36}O$ . A. H.

***o*-Nitrovanillin.** By ROBERT PSCHORR and C. SUMULEANU (*Ber.*, 1899, 32, 3405—3413).—Acetylvanillin (Tiemann and Nagai, Abstr., 1878, 579) can be advantageously prepared by shaking a solution of vanillin in the calculated amount of alkali with an ethereal solution of acetic anhydride. *o*-Nitroacetylvanillin,



prepared by dissolving acetylvanillin in well-cooled, concentrated nitric acid, crystallises from light petroleum in small, stout prisms, and melts at 85—87°; the *phenylhydrazone* crystallises in thin, reddish-brown plates and melts at 154° (corr.). *o*-Nitrovanillin,



crystallises from alcohol in minute needles and melts at 137° (corr.); the *phenylhydrazone* crystallises from acetic acid in brick-red prisms and melts at 161—162°. The *methyl ether* crystallises from dilute alcohol in long prisms, and gives a *phenylhydrazone*, which crystallises from acetic acid in saffron-yellow tablets and melts at 194° (corr.). *o*-Nitroveratric acid,  $NO_2 \cdot C_6H_4(OMe)_2 \cdot CO_2H$  [= 2 : 3 : 4 : 1], was prepared by oxidation of *o*-nitrovanillin methyl ether, and found to be identical with Matsmoto's isonitroprotocatechuic acid dimethyl ether (Abstr., 1879, 501); on reduction, it gives an *o*-aminoveratric acid identical with that prepared by Kühn (Abstr., 1895, i, 367) from hemipinimide, thus establishing the constitution of Matsmoto's acid, and the position of the nitro-group in the present series of compounds. The structure of the amino-acid was further established by preparation



of the acetyl derivative, and by converting it, through the nitrile, into hemipinic acid.

*o*-Nitrovanillin methyl ether,  $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{NO}_2$  [1 : 3 : 4 : 6], was prepared by the action of cold nitric acid on vanillin methyl ether, and is isomeric with that prepared through the acetyl compound; it crystallises from alcohol in minute, yellow needles and melts at  $132\text{--}133^\circ$  (corr.); the *phenylhydrazone* crystallises from acetic acid in glistening, reddish-brown, four-sided plates and melts at  $216\text{--}218^\circ$  (corr.). The position of the nitro-group is shown by the fact that, like the isomeride previously described, the aldehyde gives the indigo-reaction, and is therefore a derivative of *o*-nitrobenzaldehyde. On oxidation, it gives a nitroveratric acid  $[\text{CO}_2\text{H} : (\text{OMe})_2 : \text{NO}_2 = 1 : 3 : 4 : 6]$  identical with that prepared by Tiemann and Matsumoto by nitration of veratric acid; the constitution of the latter is thus established.

T. M. L.

**Condensation of Cyclic Ketones with Ethyl Succinate.** By HANS STOBBE [AND RICHARD FISCHER] (*Ber.*, 1899, 32, 3354—3356. Compare *Abstr.*, 1899, i, 900).—When an ethereal solution of cyclopentanone and ethyl succinate is left in contact with sodium ethoxide (free from alcohol) for several weeks, and is then treated with water, the ethereal solution contains ethyl succinylsuccinate, together with small quantities of indifferent substances and the aqueous alkaline solution, a mixture of sodium salts of acid esters. After acidifying, hydrolysing with barium hydroxide, and fractional separation of the barium salt thus obtained, two acids have been obtained. One of these,  $\text{C}_{14}\text{H}_{15}\text{O}_4$ , crystallises from water, melts at  $135^\circ$ , and yields a sparingly soluble barium salt; it is formed by the elimination of two mols. of water from two mols. of the ketone and one of the ethyl ester. The second acid,  $\text{C}_9\text{H}_{12}\text{O}_4$ , crystallises from benzene, water, or ether, melts and decomposes at  $205\text{--}209^\circ$ , yields a readily soluble barium salt, and is produced from one mol. of the ketone and one of the ethyl ester.

J. J. S.

**Methylcyclohexanone.** By OTTO WALLACH (*Ber.*, 1899, 32, 3338—3341).—With reference to Klages' paper on methylcyclohexanone (this vol., i, 44), it is pointed out that the constitution of this substance has been previously determined in the author's laboratory by two independent methods. The first method is one of oxidation, whereby methylcyclohexanone is converted into  $\beta$ -methyladipic acid; the second consists in transforming the ketone into *m*-bromocresol.

The action of bromine on methylcyclohexanone has also been investigated; crystalline bromo-substitution products, which furnish cresol and bromocresol by removal of hydrogen, and compounds with tear-exciting odours have been obtained; the latter probably contain bromine in the side chain. The interaction between phosphorus pentachloride and methylcyclohexanone has also been studied, and the tetrahydrochlorotoluene produced has been characterised.

G. T. M.

**Preparation of Tetrachloro- and Tetrabromo-*o*-quinones from the corresponding Tetrahaloid Guaiacols and Veratroles.** By H. COUSIN (*Compt. rend.*, 1899, 129, 967—968).—When the tetra-

chloro- and tetrabromo-guaiacols or veratroles are subjected to Zincke's reaction, that is, oxidation with nitric acid, they give rise to the corresponding tetrahaloid *o*-quinones. The yields obtained are good when the guaiacol derivatives are used, but with the veratrole compounds they are poor, owing to fuming nitric acid being necessary for the oxidation.

Tetrachloro-*o*-quinone gives with benzene a compound,  $C_6Cl_4O_2 + 3C_6H_6$ , crystallising in large, red, elongated prisms, which rapidly lose the benzene in the air, leaving the tetrachloroquinone as a violet-red powder.

T. H. P.

**Stereochemistry of Quinoneoximes.** By FRIEDRICH KEHRMANN (*Annalen*, 1899, 310, 89—111. Compare Abstr., 1899, i, 128).—[With O. KRÜGER].—3-Chlorothymoquinone [Me:O<sub>2</sub>:Cl:Pr = 1:2:5:3:4], prepared by oxidising dichlorocarvacrol with chromic acid, is volatile in steam, and crystallises from alcohol in yellow leaflets melting at 41—42°; it separates from petroleum in crystals belonging to the rhombic system [ $a:b:c = 2.8449:1:1.1390$ ]. The *oxime* decomposes at 158°, and separates from alcohol in crystals belonging to the monoclinic system [ $a:b:c = 1.5108:1:2.4862$ ;  $\beta = 118^\circ 20'$ ]. The *acetyl* and *benzoyl* derivatives of the *oxime* melt at 81—82° and 128—129° respectively.

3-Bromothymoquinone [Me:O<sub>2</sub>:Br:Pr = 1:2:5:3:4] obtained from dibromocarvacrol by oxidation, is identical with the derivative obtained from bromocarvacrolsulphonic acid (compare Abstr., 1890, 367); the crystals from petroleum belong to the monoclinic system [ $a:b:c = 2.7130:1:1.1396$ ;  $\beta = 91^\circ 51'$ ]. The *oxime* decomposes at 157—158° and crystallises in prisms belonging to the monoclinic system [ $a:b:c = 2.6233:1:3.9232$ ;  $\beta = 97^\circ 4'$ ]. The *acetyl* and *benzoyl* derivatives of the *oxime* melt at 75—76° and 130—131° respectively.

3-Iodothymoquinone [Me:O<sub>2</sub>:I:Pr = 1:2:5:3:4] has been already described, and crystallises in the monoclinic system [ $a:b:c = 2.5257:1:1.1396$ ;  $\beta = 95^\circ 20'$ ]. The *oxime* decomposes at 141—142°, and crystallises in the monoclinic system [ $a:b:c = 2.7031:1:3.7019$ ;  $\beta = 96^\circ 2'$ ]. The *acetyl* and *benzoyl* derivatives of the *oxime* melt at 99—100° and 144° respectively.

6-Chlorothymoquinone [Me:O<sub>2</sub>:Pr:Cl = 1:2:5:4:6], prepared by oxidising dichlorothymol, crystallises from alcohol in golden-yellow prisms, and melts at 39—40°; it separates from petroleum in monoclinic crystals, having the axial ratios [ $a:b:c = 2.2533:1:2.5796$ ;  $\beta = 95^\circ 22'$ ]. The *oxime* crystallises from alcohol in pale yellow prisms belonging to the monoclinic system [ $a:b:c = 2.1203:1:0.8713$ ;  $\beta = 99^\circ 36'$ ], and decomposes at 152°. The *acetyl* derivative of the *oxime* forms rhombic crystals and melts at 76—77° [ $a:b:c = 0.5767:1:0.4777$ ]. The *benzoyl* derivative separates in monoclinic crystals [ $a:b:c = 1.6793:1:1.1808$ ;  $\beta = 97^\circ 6'$ ], and melts at 126—127°.

6-Bromothymoquinone, which crystallises in the monoclinic system [ $a:b:c = 2.2284:1:2.5002$ ;  $\beta = 94^\circ 11'$ ] and melts at 46—47°, has been already described. The *oxime* also crystallises in the monoclinic system [ $a:b:c = 1.0699:1:0.8737$ ;  $\beta = 103^\circ 38'$ ]; the *acetyl* derivative

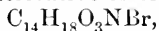
melts at  $71-72^\circ$ , and has the same axial ratios as the acetyl derivative of 6-chlorothymoquinoneoxime, and the *benzoyl* derivative, which melts at  $119-120^\circ$ , crystallises in the monoclinic system [ $a:b:c = 1.6861:1:1.1873$ ;  $\beta = 97^\circ 26'$ ].

6-Iodothymoquinone, which crystallises in the monoclinic system [ $a:b:c = 2.0164:1:0.4834$ ;  $\beta = 100^\circ 3'$ ] and melts at  $61-62^\circ$ , has been already described; the oxime is rhombic [ $a:b:c = 0.9067:1:0.3905$ ]; the acetyl derivative melts at  $67-68^\circ$ , and has the same axial ratios as the acetyl derivative of 6-chlorothymoquinoneoxime, and the *benzoyl* derivative, which melts at  $144^\circ$ , crystallises in the rhombic system [ $a:b:c = 0.6745:1:0.3799$ ].

[With M. SCHOEN].—*Chloronitrothymol* [ $\text{Me}:\text{Cl}:\text{OH}:\text{Pr}:\text{NO}_2 = 1:2:3:4:6$ ], prepared by oxidising 6-chlorothymoquinoneoxime with nitric acid, crystallises from alcohol in pale yellow, lustrous needles, and melts at  $116^\circ$ ; it is also produced when chlorine is passed into 6-nitrothymol dissolved in glacial acetic acid.

Bromonitrothymol [ $\text{Me}:\text{Br}:\text{OH}:\text{Pr}:\text{NO}_2 = 1:2:3:4:6$ ], obtained on oxidising 6-bromothymoquinoneoxime, crystallises from alcohol in yellow prisms, and melts at  $109^\circ$ ; it is also prepared by adding bromine to 6-nitrothymol dissolved in glacial acetic acid.

The *diacetyl* derivative of chloroaminocarvacrol,  $\text{C}_{14}\text{H}_{18}\text{O}_3\text{NCl}$ , obtained from 3-chlorothymoquinoneoxime by reduction with stannous chloride followed by acetylation, crystallises in long, lustrous needles, and melts at  $175^\circ$ ; it is also produced when *p*-nitrocarvacrol [ $\text{Me}:\text{OH}:\text{Pr}:\text{NO}_2 = 1:2:4:5$ ] is chlorinated, reduced, and finally acetylated. The *diacetyl* derivative of bromoaminocarvacrol,



prepared by analogous methods, crystallises in lustrous needles and melts at  $157-158^\circ$ . M. O. F.

**Halogen Derivatives of Anthragallol.** By FRANZ SLAMA (*Chem. Centr.*, 1899, ii, 966—967; from *Diss. Giessen*, 1899, 1—26).—By the action of halogens on anthragallol, the halogen enters into the ring which contains the hydroxyl groups in a similar manner to the formation of nitro-derivatives (compare Bamberger and Böck, *Abstr.*, 1897, i, 576). When bromoanthragallol is melted, or oxidised by nitric acid, benzoic acid is formed, and when melted with potassium hydroxide at  $200^\circ$  it yields tetrahydroxyanthraquinone identical with Bayer and Co.'s compound (German Patent, 86968), hence the formula of the halogen derivative is  $\text{C}_{14}\text{H}_4\text{Br}(\text{OH})_3\text{O}_2$  or 4-chloro-1:2:3-trihydroxyanthraquinone. When chlorine is passed into anthragallol suspended in glacial acetic acid, *chloroanthragallol* is formed; this crystallises in orange-red needles, melts at  $220^\circ$ , is soluble in alcohol, glacial acetic acid, or xylene, and forms a green solution in aqueous potassium hydroxide and a red in concentrated sulphuric acid. *Bromoanthragallol*,  $\text{C}_{14}\text{H}_7\text{BrO}_5$ , melts at  $212^\circ$ , decomposes when distilled in a vacuum, is oxidised by nitric acid, forming benzoic acid, and is decomposed by nitrous acid. Tetrahydroxyanthraquinone,  $\text{C}_{14}\text{H}_4\text{O}_2(\text{OH})_4$ , prepared by heating bromoanthragallol with potassium hydroxide and a little water at  $206^\circ$ , forms a sublimate consisting of green needles, and dissolves in sulphuric acid or aqueous potassium hydroxide, forming a red

solution. *Tetra-acetoxyanthraquinone*,  $C_{13}H_4O_2(OAc)_4$ , crystallises in yellow needles, melts at  $205^\circ$ , and dissolves in boiling aqueous potassium hydroxide, forming a violet-red solution, but is insoluble in the cold. *Chloroacetylchloroanthragallol*, prepared by the action of chloroacetyl chloride on chloroanthragallol, crystallises in silky, yellow needles and melts at  $189-195^\circ$ ; *chloroacetyl bromoanthragallol* forms similar crystals and melts at  $197-203^\circ$ . The products obtained by the action of chloroacetyl chloride are not, however, homogeneous compounds. When the halogen compounds are boiled with acetic anhydride, triacetyl derivatives are obtained, hence these compounds contain three hydroxyl groups. *Chlorotriacetyl anthragallol*,  $C_{14}H_4ClO_2(OAc)_3$ , crystallises in yellow needles, melts at  $187^\circ$ , and dissolves in boiling aqueous potassium hydroxide, forming a red solution, which quickly becomes green. *Bromotriacetyl anthragallol*,  $C_{14}H_4O_2Br(OAc)_3$ , crystallises in yellow needles and melts at  $178^\circ$ . *Chlorotribenzoyl anthragallol*,  $C_{14}H_4O_2Cl(OBz)_3$ , forms yellowish needles, melts at  $209^\circ$ , and dissolves in boiling aqueous potassium hydroxide, forming a green solution. *Bromotribenzoyl anthragallol*,  $C_{14}H_4O_2Br(OBz)_3$ , forms yellow crystals, melts at  $206^\circ$ , is slightly soluble in glacial acetic acid or alcohol, but insoluble in cold aqueous potassium hydroxide. E. W. W.

**Constitution of Camphor.** By LOUIS BOUEVAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1013—1019).—An account of the author's views on the constitution of camphor and its derivatives, and the researches which have led to their modification since 1892. Attempts to effect the synthesis of derivatives of camphoric acid have met with the same want of success as the experiments of Perkin (*Trans.*, 1899, 75, 909). Attempts to convert ethyl isoamylacetoacetate into ethyl isolaureonolate by the action of various dehydrating agents all failed.

N. L.

**Molecular Refraction and Dispersion and Specific Rotation of Alkyl Derivatives of Camphor.** By ALBIN HALLER and PAUL TH. MULLER (*Compt. rend.*, 1899, 129, 1005—1008. Compare *Abstr.*, 1899, i, 770, ii, 622).—The molecular refraction and dispersion, and specific rotation of the following compounds have been determined: benzylidenecamphor, piperonylidenecamphor, cuminylcamphor, ethylsaligenylcamphor, *m*-methoxybenzylcamphor and *p*-methoxybenzylcamphor. The agreement between the found and calculated values (using Brühl's and Conrady's coefficients) is much closer than in the case of the compounds of camphor with aromatic aldehydes. This difference between the two values in the latter compounds is probably due to the double linking between the camphor and aldehyde groups, which is absent in the compounds enumerated above, hence the closer agreement. H. R. LE S.

**Pulegone and Isopulegone.** By CARL D. HARRIES and GEORG ROEDER (*Ber.*, 1899, 32, 3357—3373. Compare Beckmann and Pleissner, *Abstr.*, 1891, 936; Semmler, 1893, i, 130; Wallach, 1896, i, 309; Tiemann and Schmidt, 1897, i, 198).—Pulegonehydroxylamine (*Abstr.*, 1898, i, 573) forms an *oxalate*,  $(C_{10}H_{19}O_2N) \cdot C_2O_4H_2$ , which crystallises in prismatic needles melting and decomposing at  $151-152^\circ$ .

With nitrous acid, the hydroxylamine yields a white, crystalline mass, probably the nitrosamine, which is extremely unstable; it also reacts with hydriodic acid, yielding 8-aminomenthone (compare Beckmann and Pleissner), the *oxalate* of which has been prepared; so far, the authors have not succeeded in condensing this salt with different aldehydes (compare Fischer, Abstr., 1884, 53). *Bispulegone*,  $C_{20}H_{34}O_2$ , obtained by the action of aluminium amalgam on pulegone, crystallises in needles, melts at 118—119°, and is readily soluble in benzene, ether, or acetic acid; when sodium amalgam is used in acetic acid solution, considerable quantities of menthone and of menthol are also formed. When hydrobromopulegone is boiled with alcohol and lead hydroxide as recommended by Beckmann and Pleissner, the chief product is methyleyclohexanone (compare Wallach); the same product is formed when pulegone is boiled with ethyl alcohol and basic lead acetate, or when it is distilled with quinoline. When, however, the ketone is heated on the water-bath for half an hour with methyl alcohol and basic lead nitrate, a 70 per cent. yield of *α-isopulegone* is obtained; this may be separated from unaltered pulegone by treatment in ethereal solution with aluminium amalgam and subsequent distillation in steam, and finally purified by conversion into its oxime melting at 120—121°; the latter is identical with the oxime obtained by Tiemann and Schmidt. *α-Isopulegone* is a colourless oil distilling at 98—100° under 13 mm. pressure, and has a sp. gr. 0.9192 at 19.5°, and a rotatory power  $\alpha_D - 7.8^\circ$ , but when kept for some time in contact with dilute sulphuric acid, it becomes inactive; its semicarbazone,  $C_{11}H_{19}ON_3$ , crystallises from dilute alcohol in needles melting and decomposing at 173—174°. When an alcoholic solution of *α-isopulegone* is left for 24 hours in contact with baryta water, it is completely converted into ordinary dextrorotatory pulegone.

According to the authors, the isopulegone obtained by Tiemann and Schmidt's method yields a *semicarbazone* melting at 183° and an *oxime* melting at 143°; they therefore term it *β-isopulegone*. According to recent experiments by Tiemann, a mixture of the *α*- and *β*-compounds is obtained by his method; these are probably the two inactive forms of the constitution  $CHMe \begin{smallmatrix} \text{CH}_2 - CO \\ \text{CH}_2 \cdot CH_2 \end{smallmatrix} > CH \cdot CMe : CH_2$ , whereas pulegone is  $CHMe \begin{smallmatrix} \text{CH}_2 - CO \\ \text{CH}_2 \cdot CH_2 \end{smallmatrix} > C : CMe_2$ . J. J. S.

**Camphenylone.** By EDMOND E. BLAISE and G. BLANC (*Compt. rend.*, 1899, 129, 886—889. Compare Abstr., 1899, i, 627, 629, 820).—If Jagelki's formula for camphoceanic acid, and Bredt's formula for isolauronic acid are correct, then the nitriles of these two acids on reduction should give one and the same amine. This, however, is not the case, as the following results show.

Camphenylone prepared by the action of nitric acid vapours on camphene at 0°, was purified by converting it into its *semicarbazone* melting at 224°, which, on treatment with hydrochloric acid, gives pure camphenylone, melting at 37°. The *oxime* readily sublimes and melts at 109—110°, and on dehydration with acetyl chloride, gives *camphoceanonitrile*, boiling at 220—230°, and an *iso-oxime* melting

at 165°. Camphoceanonitrile, on reduction with sodium and absolute alcohol, gives an unsaturated *base*, which boils at 204—205° and readily takes up carbon dioxide. The *hydrochloride* of this base is a white powder, which darkens at 195° and decomposes at 225°, and when treated with potassium cyanate gives a substituted *carbamide*,  $C_9H_{15} \cdot NH \cdot CO \cdot NH_2$ , crystallising in micaceous plates, which melt at 118° and are only slightly soluble in cold, but readily in hot, benzene. The *oxamide*, prepared by the action of ethyl oxalate on the base, forms needles which melt at 148°, and are very slightly soluble in alcohol; its *platinichloride* is a yellow powder insoluble in alcohol and in water. From the mother liquor of the hydrochloride of the above unsaturated base, the hydrochloride of an isomeric *base* was isolated; this boils at 195°, its *hydrochloride* melts at 175—176°, the *oxamide* and substituted *carbamide* at 106—107°, and the *picrate* at 178°.

The authors conclude that the trimethylcyclopentane group is not present in camphenylone and its derivatives. H. R. LE S.

**Ethereal Oils.** By SCHIMMEL AND Co. (*Chem. Centr.*, 1899, ii, 879—881; from *Geschäftsber.*, October, 1899).—There are two kinds of commercial oil of citronella, differing only slightly in physical properties and chemical composition. The ordinary oil “Lana Batu” contains less geraniol and citronellal than the better oil “Maha pangiri,” which is richer in compounds capable of forming acetyl derivatives. A sample of the former oil having a sp. gr. 0.908 at 15°, rotatory power  $-9^{\circ}36'$ , and containing 61.1 per cent. of geraniol and citronellal, was found not only to contain camphene, dipentene, and limonene, but also two sesquiterpenes; the one boils and decomposes at 260—270° under the ordinary pressure, and at 157° under 15 mm. pressure, has sp. gr. 0.8643 at 15°, rotatory power  $+1^{\circ}28'$ , and refractive index 1.51849 at 15°, whilst the other boils at 272—275° under the ordinary pressure, at 170—172° under 16 mm. pressure, has sp. gr. 0.912 at 15°, and rotatory power  $+5^{\circ}50'$ . The former terpene resinifies very easily, and this property explains the fact that, whilst many oils form clear solutions when dissolved in small quantities of 80 per cent. alcohol, they give turbid solutions when treated with four or more parts of the same alcohol.

The oil of citronella contained traces of linalool, about 1 per cent. of borneol and methyleugenol.

Another sample of citronella oil contained 33 per cent. of geraniol, 28 of citronellal, and 8 of methyleugenol.

The aqueous distillate obtained from oil of cumin contains methyl alcohol and furfuraldehyde. The yellowish colour of the former appears to depend on the presence of diacetyl; this is also the case with the methyl alcohol obtained from oil of cloves. The aqueous distillate of musk oil also contains furfuraldehyde.

About 9 per cent. of damascenine was extracted from nigella oil by shaking with tartaric acid and decomposing the tartrate with sodium carbonate; this compound has a blue fluorescence, solidifies in the cold, boils at 117° under 10 mm. pressure, and has a saponification number 277.4. From the alkaline liquid left after decomposing the

tartrate, a fluorescent acid, probably an amido-acid, was isolated; it crystallises from ether in prisms, is easily soluble in water, and forms a slightly soluble platinichloride. The presence of methoxy-groups in damascenine was confirmed.

Mustard oil always contains carbon disulphide, hence the determinations of sulphur do not exactly correspond with the amount of allylthiocarbimide present.

The fresh flowering plants and the roots of *Viola tricolor*, when distilled, yield 0.00859 per cent. of an ethereal oil, which consists mainly of methyl salicylate. E. W. W.

**Rhamninase and Xanthorhamnin.** By CHARLES TANRET and GEORGES TANRET (*Bull. Soc. Chim.*, 1899, [iii], 21, 1073—1075. Compare this vol., i, 78).—Rhamninase is precipitated by alcohol from the cold water extract of the fruit of *Rhamnus infectoria* as a pasty mass containing 28—50 per cent. of solid matter; it is very soluble in water, and its activity does not diminish appreciably on keeping. The dry substance contains mineral salts (17 per cent.), substances coagulated by heat (53 per cent.), and galactan. A temperature of 70° is most favourable to the action of the enzyme, which is destroyed at 85°.

When xanthorhamnin is heated with water at 50°, a pale yellow, crystalline precipitate is gradually formed, quite different from that produced by the action of rhamninase. This substance is a new glucoside, which has a composition very similar to that of xanthorhamnin, but differs from it in not being acted on by rhamninase and in yielding a larger proportion of rhamnose on hydrolysis. The solution, from which the insoluble glucoside has been deposited, contains a substance, *xanthorhamnein*, which differs from xanthorhamnin in being more soluble and in having a higher rotatory power ( $[\alpha]_D +5^\circ$  instead of  $+3^\circ.75$ ). Schützenberger's observations on the existence of two modifications of xanthorhamnin are thus confirmed.

N. L.

**Rhubarb and its Active Constituents.** By ALEXANDER TSCHIRCH (*Arch. Pharm.*, 1899, 237, 632—637).—It is pointed out that Hesse (this vol., i, 40) is incorrectly informed as to the species of rhubarb cultivated in England for pharmaceutical purposes; also that chrysophanic acid has lately been shown to have a purgative action, although to a less degree than alochrysin, and still less than emodin.

C. F. B.

**Colouring Matter of Digitalis.** By L. ALPHONSE ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1899, 129, 889—890).—The substance  $C_{16}H_{12}O_4$  was isolated from *Digitalis lutea* by a process analogous to that employed for the extraction of the yellow colouring matter from *Artemisia absinthium* (Abstr., 1899, i, 301). It crystallises in beautiful, yellow needles, melts at 217—218°, and dissolves in ethyl alcohol, chloroform, or amyl alcohol; in alkalis, it is soluble, forming solutions of a beautiful red colour. Hydrochloric acid is without action on it, and it does not form a compound with phenylhydrazine, neither does it give a reducing sugar. When treated with hydrochloric acid or potash, neither catechol nor phloroglucinol is

produced, which shows that the substance is not identical with the digitoflavone of Fleischer.

H. R. LE S.

**Active Constituents of the Wallflower.** By MORITZ REEB (*Chem. Centr.*, 1899, ii, 917—918; from *Arch. exp. Path. Pharm.*, **43**, 130—148. Compare Abstr., 1899, i, 378).—The physiological action of cheiranthin resembles that of the digitalis compounds.

**Cheirinine**,  $C_{18}H_{35}O_{17}N_3$ , obtained from the alcoholic extract of the seeds of the wallflower, crystallises in small, colourless needles, melts at 73—74°, and is soluble in warm water, alcohol, ether, chloroform, or ethyl acetate. The aqueous solution is neutral and gives precipitates with the ordinary alkaloidal reagents. The physiological action of cheirinine resembles that of quinine.

The seeds also contain choline.

E. W. W.

**Alkaloids of the Seeds of *Lupinus Angustifolius* and of *Lupinus Perennis*, var. *Polyphyllus*.** By JÜRGEN CALLEN (Arch. Pharm., 1899, 237, 566—595. Compare Siebert, Soldaini, Davis, Berend, and Gerhard, Abstr., 1892, 223; 1893, i, 759; 1896, i, 193; 1897, i, 174, 645, 646).—No other alkaloid, in addition to *d*-lupanine, could be isolated from the seeds of blue and of perennial lupins; the yield of alkaloid is seven times as great in the case of the latter plant.

No new product, but only unchanged lupanine, could be isolated when lupanine was boiled with acetyl chloride, heated with fuming hydrochloric acid at 150—180°, heated with potassium permanganate and dilute sulphuric acid on the water-bath, allowed to remain with hydrogen peroxide at the ordinary temperature and in the dark, heated on the water-bath with water and yellow mercuric oxide, or with 10 per cent. nitric acid, treated in cold alcoholic solution with metallic sodium, heated at 200° with acetic anhydride or with dilute sulphuric acid, or on the water-bath with concentrated sulphuric acid, or at 150° with fuming hydriodic acid and amorphous phosphorus.

From the product of the action of bromine on lupanine hydrochloride in alcoholic solution, no alkaloid could be isolated (except unchanged lupanine) other than  $C_8H_{15}ON$  (Davis; Soldaini,  $C_8H_{13}ON$ , *loc. cit.*). The *platinichloride*,  $(C_8H_{15}ON)_2 \cdot H_2PtCl_6 + 1\frac{1}{2}H_2O$ , decomposed at 200°; the base is a tertiary one, for it does not unite with phenylthiocarbimide, and it forms a methiodide, the *platinichloride*, corresponding with which,  $2(C_8H_{15}ONMe)_2PtCl_6 + 6H_2O$ , decomposes just above 200°.

C. F. B.

**Alkaloids from the Salamander.** By EDWIN S. FAUST (*Chem. Centr.*, 1899, ii, 718—719; from *Arch. exp. Path. Pharm.*, **43**, 83—92. Compare Abstr., 1899, i, 380).—Samandarine sulphate,



which has been prepared in large quantities, crystallises either in small, anhydrous needles, usually arranged in small tufts or star-shaped groups, or occasionally in large, hydrated needles. It has a specific rotatory power  $[\alpha]_D -53.69^\circ$ , and gives a blue coloration when boiled with concentrated hydrochloric acid. When the platinichloride



is dried over sulphuric acid, it loses hydrogen chloride, and forms the compound  $(C_{26}H_{40}ON_2)_2PtCl_4$ . Experiments with dogs showed that doses of 0.0007—0.0009 gram per kilogram of body weight are fatal, the symptoms of samandarine poisoning being very similar to those of rabies.

The fire salamanders also contain another alkaloid, *samandaridine*, which appears to be present in larger quantities than samandarine. The *sulphate*,  $(C_{20}H_{31}ON_2)_2SO_4$ , crystallises in rhombic plates, is very slightly soluble in water or alcohol, is optically inactive, and has the same pharmacological action as samandarine sulphate, but to a less degree. When boiled with hydrochloric acid, it behaves like samandarine, and on distillation with zinc dust yields isoquinoline.

E. W. W.

**Behaviour of Iodoform and Chloroform with Strychnine.** By PERRY F. TROWBRIDGE (*Arch. Pharm.*, 1899, 237, 622—625).—The compound  $3C_{21}H_{22}O_2N_2 \cdot CHI_3$  (Lextreit, Abstr., 1881, 748) is formed even when 1 mol. of iodoform is allowed to react with 1 mol. of strychnine; the two substances were allowed to remain together in chloroform solution at the ordinary temperature for a day, and the compound then precipitated with ether. When it is boiled with alcohol, another compound,  $2C_{21}H_{22}O_2N_2 \cdot CHI_3$ , is obtained; this is also a reddish-brown, crystalline powder, which decomposes and melts at about 220°.

When a chloroform solution of strychnine is subjected to prolonged heating at 150°, a crystalline compound,  $C_{21}H_{22}O_2N_2 \cdot HCl \cdot CHCl_3$ , is obtained; this loses its chloroform partly at the ordinary temperature and entirely at 100°.

C. F. B.

**Action of Methylene Iodide on Strychnine.** By PERRY F. TROWBRIDGE (*Arch. Pharm.*, 1899, 237, 617—622).—When strychnine and methylene iodide are heated together in methyl alcoholic solution, or allowed to remain in chloroform solution at the ordinary temperature, a white, crystalline compound,  $CH_2I \cdot C_{21}H_{22}O_2N_2 \cdot I$ , is obtained; this melts at 212°, and readily exchanges one of its iodine atoms for chlorine, &c. The corresponding *chloride*,  $CH_2I \cdot C_{21}H_{22}O_2N_2 \cdot Cl$ , *aurochloride*, *platinichloride*, *mercurichlorides*,  $CH_2I \cdot C_{21}H_{22}O_2N_2 \cdot Cl \cdot HgCl_2$ , and with  $1\frac{1}{2}HgCl_2$ , *bromide*, *hydrogen sulphate*, *hydrogen chromate*, and *nitrate* were prepared and analysed.

C. F. B.

**Action of Iodine on Piperidine, Tetrahydroquinoline, and Tetrahydroisoquinoline.** By ERNST SCHMIDT (*Arch. Pharm.*, 1899, 237, 561—565).—When tetrahydroquinoline is heated with iodine and alcohol in a closed vessel in the steam-bath, it is oxidised to quinoline. Tetrahydroisoquinoline, however, yields but little isoquinoline under similar circumstances, and piperidine does not yield pyridine.

C. F. B.

**6-Aminoquinoline and its Derivatives.** By CHR. A. KNEUFEL (*Annalen*, 1899, 310, 75—88. Compare Abstr., 1896, i, 391).—6-Aminoquinoline, prepared by reducing 6-nitroquinoline in alcohol with iron borings, yields the *hydrochloride* in golden-yellow needles

melting at  $109^{\circ}$ ; the dihydrochloride is insoluble in hot alcohol and melts at  $250^{\circ}$ .

*Thionyl-6-aminoquinoline*,  $C_9NH_6 \cdot N : SO$ , crystallises in small, yellow needles, and melts at  $64-65^{\circ}$ ; it is gradually decomposed by hot water, yielding sulphur dioxide; *6-aminoquinolinethionamic acid*,  $C_9NH_6 \cdot NH \cdot SO_2H$ , melts at  $124^{\circ}$ .

*6-Quinylurethane*,  $C_9NH_6 \cdot NH \cdot CO_2Et$ , crystallises from hot alcohol in brownish plates, and melts at  $168^{\circ}$ ; the *hydrochloride* forms white needles.

*6-Acetylaminquinoline*,  $C_9NH_6 \cdot NHAc$ , crystallises from hot water in white needles melting at  $138^{\circ}$ , and the *hydrochloride* also forms needles; the *salicylate*, *tartrate*, and *methiodide* melt at  $140^{\circ}$ ,  $226^{\circ}$ , and  $268^{\circ}$  respectively.

*6-Benzoylaminoquinoline*,  $C_9NH_6 \cdot NHBz$ , crystallises in yellowish needles and melts at  $169^{\circ}$ ; the *sulphate*, *hydrochloride*, and *nitrate* are well crystallised substances.

*6-Quinolinehydrazine*,  $C_9NH_6 \cdot NH \cdot NH_2$ , has not been obtained in crystalline form, but derivatives are easily obtained. The *benzylidene* compound separates from water in long, reddish-yellow needles, and from alcohol in deep red cubes melting at  $203^{\circ}$ ; the *semicarbazide* derivative melts at  $234^{\circ}$ , and the *pyruvic hydrazone* crystallises in orange-red needles melting at  $201^{\circ}$ .

*6-Azoquinoline*,  $N_2(C_9NH_6)_2$ , a bye-product in the preparation of 6-aminoquinoline, crystallises in lustrous, orange red needles and melts at  $248^{\circ}$ . *6-Azoxydiquinoline*,  $C_{15}H_{10}ON_4$ , prepared by heating 6-nitroquinoline with sodium methoxide in methyl alcohol, crystallises from alcohol in dark violet needles and does not melt below  $280^{\circ}$ ; the solution in sodium hydroxide is deep green. *6-Azodiquinoline*,  $C_{15}H_{10}N_4$ , obtained when the foregoing substance is distilled with iron borings in an atmosphere of hydrogen, crystallises from xylene in yellow needles, infusible below  $280^{\circ}$ .

*Dimethylaminobenzene-6-azoquinoline*,  $C_9NH_6 \cdot N : N \cdot C_6H_4 \cdot NMe_2$ , prepared from diazotised 6-aminoquinoline and dimethylaniline, crystallises from alcohol in lustrous, steel-blue needles. *Benzene-6-diazo-aminoquinoline*,  $C_9NH_6 \cdot NH \cdot N : NPh$ , formed on adding diazobenzene chloride to aminoquinoline, crystallises in long, orange-yellow needles, melting at  $142$ ; the *hydrochloride* is crystalline, and the *methiodide* melts at  $220^{\circ}$ .  
M. O. F.

**4-Hydroxycarbostyryl from Anthranilic Acid.** By HUGO ERDMANN (*Ber.*, 1899, 32, 3570—3573. Compare Baeyer and Bloem, *Abstr.*, 1883, 196, and Camps, this vol., i, 115).—4-Hydroxycarbostyryl is obtained when methyl anthranilate (*Abstr.*, 1899, i, 621) is heated on the water-bath with ethyl acetate and metallic sodium for some three hours. The product is treated with ice-cold acetic acid and then shaken with water and ether, when the carbostyryl begins to separate. The ethereal filtrate contains *methyl diacetylanthranilate*,  $NAc_2 \cdot C_6H_4 \cdot CO_2Me$ , together with more hydroxycarbostyryl. This diacetyl derivative crystallises in glistening prisms melting at  $180^{\circ}$ , has a burning taste, dissolves in boiling alkalis, and is decomposed by dilute mineral acids.

Acetylanthranilic acid melts at  $185^{\circ}$ , and its methyl ester at  $101^{\circ}$ ; acetylsalicylic acid melts at  $132^{\circ}$ , and its methyl and phenyl esters at  $49^{\circ}$  and  $98^{\circ}$  respectively.

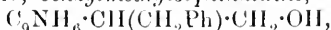
J. J. S.

**Action of Aldehydes on Quinoline Derivatives containing a Methyl or Methylene Group in Position 2 or 4.** By WILHELM KOENIGS (*Ber.*, 1899, 32, 3599—3613).—When benzaldehyde is heated with quinaldine (2 mols.) in presence of zinc chloride at  $150$ — $160^{\circ}$ , a small quantity of benzylidenequinaldine (Doebner and von Miller, *Abstr.*, 1885, 1080) is formed together with a larger proportion of *benzylidenediquinaldine*,  $\text{CHPh}(\text{CH}_2\cdot\text{C}_9\text{NH}_6)_2$ , the *hydrochloride* of which crystallises from absolute alcohol containing hydrochloric acid in beautiful, colourless plates\*; the *nitrate* and *sulphate* form colourless crystals, whilst the *platinichloride*, with  $3\text{H}_2\text{O}$ , consists of yellow prisms and melts and decomposes at  $240^{\circ}$ . The *base* is a colourless, soft resin and cannot be obtained crystalline. When heated with benzaldehyde in presence of zinc chloride for 7—8 hours at  $160$ — $170^{\circ}$ , it yields a large quantity of resin, together with a small amount of benzylidenequinaldine, the expected tetramethylene derivative,  $\text{C}_9\text{NH}_6\cdot\text{CH} < \begin{smallmatrix} \text{CHPh} \\ \text{CHPh} \end{smallmatrix} > \text{CH}\cdot\text{C}_9\text{NH}_6$ , apparently not being formed.

*Benzylidenedilepidine*, prepared in the same manner as the corresponding quinaldine derivative, crystallises from alcohol in colourless prisms and melts and decomposes indefinitely between  $110^{\circ}$  and  $127^{\circ}$ ; the *hydrochloride*, with  $2\text{H}_2\text{O}$ , crystallises in concentric aggregates of needles, whilst the *platinichloride*, with  $6\text{H}_2\text{O}$ , forms a flocculent mass of yellow needles.

*Benzylmethylollepidine*,  $\text{C}_9\text{NH}_6\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{OH}$ , prepared by heating benzyllepidine with 40 per cent. aqueous formaldehyde in a sealed tube for 45 hours at  $100^{\circ}$ , crystallises from benzene in colourless, pointed prisms, and melts at  $150^{\circ}$ ; the *platinichloride* forms a yellowish, crystalline mass of leaflets. The *base* is not further acted on by heating with formaldehyde for 9 hours at  $140^{\circ}$ , and is not changed by similar treatment with benzaldehyde for 10 hours at  $180$ — $200^{\circ}$ .

When benzylquinaldine is heated with 40 per cent. aqueous formaldehyde for 38 hours, *benzylmethylolquinaldine*,



crystallising from ether in prisms or plates and melting at  $113$ — $114^{\circ}$ , is formed together with *benzylidimethylolquinaldine*,

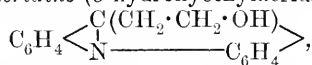


which crystallises from alcohol in colourless prisms, melts at  $141$ — $142^{\circ}$ , and yields a crystalline *hydrochloride* which sinters at  $185^{\circ}$  and melts and decomposes at  $190^{\circ}$ ; the *bases* were separated by means of their *oxalates*. Chloral condenses with benzylquinaldine in the same manner as formaldehyde, a crystalline *compound* melting at  $173^{\circ}$  being obtained. An attempt to obtain benzylquinaldine by the interaction of benzyl alcohol with quinaldine gave no result. Benzylidenequinaldine does not react with formaldehyde.

\* The original gives  $156^{\circ}$  and also  $218^{\circ}$  as the melting point of benzylidenediquinaldine hydrochloride.

Since lepidine combines with only two mols. of formaldehyde, whereas quinaldine combines with three (Abstr., 1898, i, 74 and 389), and benzyllepidine with one, although benzylquinaldine unites with two, it would appear that the benzene nucleus in the ortho-position to the methyl radicle of lepidine exercises a stereochemical, inhibiting effect; this hypothesis is, however, weakened by the fact that 5-methyl-acridine, which contains two benzene nuclei adjacent to the active methyl radicle, condenses with 2 mols. of formaldehyde but 5-ethyl-acridine, in which one of the active hydrogen atoms is replaced by a methyl radicle with only one; acridine itself does not react with formaldehyde, yet 3-methyl-2-ethylquinoline condenses with one mol. of formaldehyde, and thus behaves like benzyllepidine.

*Methylol-5-methylacridine* (5-hydroxyethylacridine),



the principal product obtained on heating 5-methylacridine with dilute alcoholic formaldehyde, is a yellow, amorphous substance, which melts at 115—125° and yields a *hydrochloride* crystallising in yellow needles; with it there is formed a small quantity of *dimethylol-5-methylacridine*,  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}$ , which crystallises from alcohol in sulphur-yellow needles and melts at 194°. *Methylol-5-ethylacridine*,

$\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{C}(\text{CHMe} \cdot \text{CH}_2 \cdot \text{OH}) \\ | \\ \text{N} \end{array} \right\rangle \text{C}_6\text{H}_4$ , obtained similarly from 5-ethyl-

acridine, separates from ethyl acetate in stout, yellow, lustrous crystals and melts at 183°; the *aurichloride* forms yellow crystals, and the *platinichloride* orange-yellow needles which melt and decompose at 225°.

Although cinchonine and conchicine do not interact with formaldehyde at 130—140°, the corresponding deoxy-bases condense with 1 mol. of the aldehyde at 100°; it thus appears that the alkaloids contain the lepidine complex  $\text{C}_9\text{NH}_6 \cdot \text{CH}(\text{OH}) \cdot \text{C}$ , and the deoxy-bases the group  $\text{C}_9\text{NH}_6 \cdot \text{CH}_2 \cdot \text{C}$ . The *platinichloride*,



of *methyloldeoxyconchicine* darkens at 215°, but does not melt at 270°; the base is amorphous, and the other salts, with the exception of the *picrate*, are similar in nature. *Methyloldeoxycinchonine*, and its *platinichloride*,  $\text{C}_{20}\text{H}_{24}\text{ON}, \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , resemble the corresponding cinchonine derivatives.

Papaverine interacts with formaldehyde at 100°, with elimination of  $11\text{H}_2\text{O}$ , to form *methylenepapaverine*,  $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}$ , which crystallises from alcohol, on adding ether, in colourless aggregates of needles, melts at 155—156°, and yields a yellow, crystalline *platinichloride* melting and decomposing between 150° and 180°; the *hydrochloride* sinters at 105°, melts at 110°, and decomposes at 130—140°; the *hydrobromide* melts at 110° and decomposes at 120°, whilst the *picrate* sinters at 100° and melts at 115°.

W. A. D.

**Amino-derivatives of  $\alpha$ -Phenylbenzothiazole.** By OTTO KUM (Ber., 1899, 32, 3532—3538. Compare Abstr., 1899, i, 647 and 943). —*Dinitrophenyl thiobenzoate*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{S} \cdot \text{COPh}$  [ $\text{S} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4$ ], can be prepared by the Schotten-Baumann method from dinitro-

phenyl mercaptan and benzoyl chloride, but more readily by mixing alcoholic solutions of chlorodinitrobenzene and potassium thiobenzoate; it crystallises from dilute acetone in long, glistening, yellow needles, melts at 111—112°, and is readily hydrolysed to dinitrophenyl mercaptan and benzoic acid; tetranitrodiphenyl sulphide is also produced, especially when the alcoholic solutions are heated. 1-Phenyl-4-aminobenzothiazole,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{S} \\ \text{N} \end{smallmatrix} > \text{CPh}$ , prepared by reducing the preceding compound by Nietzki's method (Abstr., 1897, i, 277), melts at 201—202°, forms yellowish-green crystals, and gives yellow solutions with a greenish fluorescence, but forms a white, sparingly soluble sulphate. The acetyl derivative crystallises from dilute alcohol in glistening, white needles, melts at 192—193°, and shows a slight violet fluorescence in solution.

p-Nitrothiobenzoic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{SH}$ , crystallises from dilute hydrochloric acid in long, slender, yellowish-white needles and melts at 90—95°; the disulphide crystallises from dilute acetone in large, glistening, yellowish-white leaflets, melts at 182—183°, and is reconverted into dinitrothiobenzoic acid by warming with alcoholic potash; the dinitrophenyl ester crystallises from acetone or acetic acid in glistening, yellowish-white flakes, melts at 139—140°, and is hydrolysed by aqueous potash to dinitrophenylmercaptan and p-nitrobenzoic acid.

1-p-Aminophenyl-4-aminobenzothiazole,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{S} \\ \text{N} \end{smallmatrix} > \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , prepared by reducing the trinitro-ester, crystallises from dilute acetone or alcohol in long, yellow, glistening needles, melts at 237—238°, and closely resembles the corresponding oxazole, but does not form an insoluble hydrochloride, and shows a yellowish-green fluorescence in solution; the acetyl derivative crystallises from dilute alcohol in reddish-white, glistening needles, melts at 272—273°, and shows an intense reddish-violet fluorescence in solution.

T. M. L.

Methyl-o-anisidine, Methyl-o-aminophenol and their Oxidation Products (6 Methylphenoxazine-2:3 quinone). By EMIL DIEFOLDER (*Ber.*, 1899, 32, 3514—3528).—When o-nitroanisole is reduced with tin and hydrochloric acid, a mixture of o-anisidine and chloroanisidine [ $\text{OMe} : \text{NH}_2 : \text{Cl} = 1 : 2 : 5$ ] is produced (Herold, Abstr., 1882, 1287; Reverdin and Eckard, this vol., i, 28), which is best separated by conversion into the formyl derivatives. Formyl-o-anisidine crystallises from dilute alcohol in long, colourless needles, melts at 83·5°, and dissolves in hot water and organic solvents. 5-Chloro-2-formyl-aminoanisole crystallises from alcohol in thin, colourless tablets, melts at 177—178°, is less soluble than the preceding compound, and is hydrolysed by boiling sodium hydroxide solution. Methyl-o-anisidine, prepared by methylating formyl o-anisidine, boils at 141—143° under 46—47 mm. pressure, and solidifies to long prisms which melt at 33—33·5°.

Benzenesulphon-o-anisidine crystallises from alcohol and from hot water, and melts at 89°; the sodium derivative is readily soluble in water, but is precipitated in white needles by strong sodium hydroxide. Benzenesulphonmethyl-o-anisidine crystallises from a mixture of ether

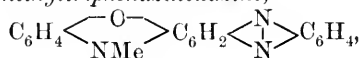
and light petroleum in well formed tablets and prisms, and melts at 60°.

*o*-Methoxyphenylglycine, when purified, melts at 153°, and crystallises in white, flat needles (compare Vater, Abstr., 1884, 1144).

*Methyl-o-nitrosoaminophenol*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NO}$ , crystallises from dilute alcohol in needles, darkens at 100°, and decomposes at 121°, dissolves readily in hot water and dilute sodium hydroxide solution, and gives Liebermann's reaction, but could not be converted into a paranitroso-compound.

*5-Methylphenoxazine-2:3-quinone*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O} & \text{---} & \text{C}:\text{CH}\cdot\text{CO} \\ & \text{NMe}\cdot & \text{C}:\text{CH}\cdot\text{CO} \end{smallmatrix}$ , prepared by oxidising methyl-*o*-aminophenol with potassium ferricyanide, melts with decomposition at 212–213°, separates from chloroform in dark-red crystals with a green shimmer, and gives a greenish-blue coloration with stannous chloride; its constitution is established by hydrolysis with sodium hydroxide to methyl-*o*-aminophenol and a dihydroxy-*o*-quinone, which passes into Nietzki and Schmidt's *p*-dihydroxy-*p*-quinone; when the latter is condensed with methyl-*o*-aminophenol, a small amount of the phenoxazinequinone appears to be reproduced.

*5-Methylphenoxazine-2:3-quinonemonoxime* is a reddish-brown, micro-crystalline powder which dissolves in dilute sodium hydroxide solution, but is hydrolysed by heating with mineral acids; it darkens at 185° and melts, with decomposition, at 200–201°; the dioxime could not be isolated in a pure state. With *o*-aminophenol, the quinone gives Seidel's triphenodioxazine (Abstr., 1890, 490). With *o*-phenylenediamine, it gives *N*-methyltriphenazinoxazine,



or, possibly,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{NMe} \end{smallmatrix}\text{C}_6\text{H}_2\begin{smallmatrix} \text{N} \\ \diagdown \quad \diagup \\ \text{N} \end{smallmatrix}\text{C}_6\text{H}_4$ , which crystallises from a mixture of benzene and absolute alcohol in orange-yellow needles, melts at 250°, sublimes with partial decomposition at higher temperatures, dissolves in organic solvents, giving yellow, fluorescent solutions, and in sulphuric acid with a blue coloration. With *o*-aminodiphenylamine and hydrochloric acid, the quinone gives *N*-methyltriphenoxazinephenylazonium chloride,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{NMe} \end{smallmatrix}\text{C}_6\text{H}_2\begin{smallmatrix} \text{N} \\ \diagdown \quad \diagup \\ \text{NPhCl} \end{smallmatrix}\text{C}_6\text{H}_4$ , or  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}\text{C}_6\text{H}_2\begin{smallmatrix} \text{N} \\ \diagdown \quad \diagup \\ \text{NPhCl} \end{smallmatrix}\text{C}_6\text{H}_4$  (compare Witt, Abstr., 1887, 729), which separates in small, bronzy needles and dissolves in water or alcohol to violet-blue solutions; the azonium base dissolves in benzene to a reddish, fluorescent solution; the *platinichloride* is a blue, microcrystalline precipitate soluble in hot water. T. M. L.

**Action of Nitrous Acid on the Leuco-base,  $\text{C}_{18}\text{H}_{24}\text{N}_2$ .** By AUGUSTE TRILLAT (*Compt. rend.*, 1899, 129, 1242–1243).—Unsymmetrical tetramethyldiaminodiphenylethane (Abstr., 1899, i, 615), when treated with sodium nitrite in cold hydrochloric acid solution, yields *p*-nitrodimethylaniline. A similar result is obtained with the leuco-bases derived from methane. G. T. M.

**Constitution of Metallic Salipyrines (Metallic Antipyrine-salicylates).** By EDOUARD BOURGEOIS (*Rec. Trav. Chim.*, 1899, 18, 451—456).—Objections are taken to Schuyten's views (this vol., i, 57) as to the structure of metallic salipyrines. T. H. P.

**History of Diazonium Salts.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 3633—3635. Compare Abstr., 1899, ii, 685 and 750).—A reply to Hantzsch (this vol., i, 126). The diazonium perbromide constitution,  $\text{NPhBr}_2\text{N}$ , for the perbromides of diazonium salts was only suggested by Hantzsch after the ammonium formula for the radicle  $\text{PhN}_2$  had been substantiated. The solubility of the diazonium carbonates and the physico-chemical evidence as to the nature of the ion of diazonium salts, merely confirm the author's views on the ammonium theory of the constitution of these compounds. G. T. M.

**Action of Aromatic Nitroso-derivatives on *as*-Alkyl Aromatic Hydrazines.** By EUGEN BAMBERGER and ARMAND STIEGELMANN (*Ber.*, 1899, 32, 3554—3560. Compare Abstr., 1896, i, 222).—The production of diazohydroxyaminobenzene,  $\text{NPh:N}\cdot\text{NPh}\cdot\text{OH}$ , from nitrosobenzene and phenylhydrazine, is probably preceded by the direct addition of the constituents to form a compound,  $\text{OH}\cdot\text{NPh}\cdot\text{NH}\cdot\text{NHPh}$ , which, by the loss of two atoms of hydrogen, yields diazohydroxyaminobenzene. This conclusion is supported by the behaviour of nitrosobenzene towards unsymmetrical phenylmethylhydrazine. When the two are brought together, the chief product is benzeneazomethyl-aniline oxide,  $\text{O:NPh:N}\cdot\text{NMePh}$  or  $\text{O} < \begin{smallmatrix} \text{NPh} \\ | \\ \text{N}\cdot\text{NMePh} \end{smallmatrix}$ , and it is probably formed by the loss of two atoms of hydrogen from the direct additive compound  $\text{OH}\cdot\text{NPh}\cdot\text{NH}\cdot\text{NHPh}$ . A secondary product formed in the same reaction is diazomethylaminobenzene (benzeneazomethylanilide),  $\text{NPh:N}\cdot\text{NMePh}$ , formed by the elimination of water from the additive compound. Other bye-products are also formed, mainly by the action of the hydrogen from the intermediate additive compound. The azoamine oxides, as a group, crystallise readily in yellow-coloured crystals which are very stable. They differ from azoamines (Abstr., 1898, i, 20) in that they give no coloration with naphthylamine acetate, but readily give Liebermann's reaction. When reduced, they yield diazoamines, primary and secondary aromatic amines, azo-, azoxy-, and hydrazo-compounds, hydrazine, and ammonia.

*Benzeneazomethylaniline oxide* crystallises in glistening, sulphur-yellow needles melting at  $72^\circ$ , and is readily soluble in most organic solvents with the exception of light petroleum. When reduced, it yields diazomethylaminobenzene, aniline, methylaniline, ammonia, and unsymmetrical phenylmethylhydrazine.

*Benzeneazodiphenylamine oxide*,  $\text{O:NPh:N}\cdot\text{NPh}_2$ , obtained together with phenylhydroxylamine, and probably diphenylamine, by the action of nitrosobenzene on unsymmetrical diphenylhydrazine, crystallises in sulphur-yellow needles, melts at  $128.5$ — $129^\circ$ , and is soluble in most organic solvents, including hot light petroleum.

*p*-Bromobenzeneazomethylaniline oxide,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NO:N}\cdot\text{NMePh}$ , crystallises in brass yellow plates melting at  $77$ — $78^\circ$ , and is only sparingly

soluble in cold light petroleum. *p*-Bromobenzeneazodiphenylamine oxide is formed, together with *p*-bromophenylhydroxylamine and *p*-dibromoazoxybenzene, by the action of *p*-bromonitrosobenzene on diphenylhydrazine; it crystallises in golden-yellow needles melting at 119—120°. J. J. S.

**Nitro-derivatives of Azo-, Azoxy-, and Hydrazo-benzene.** By ALFRED WERNER and EDMUND STIASNY (*Ber.*, 1899, 32, 3256—3282).—The details which follow show that nearly all the results obtained by Janovsky (*Abstr.*, 1886, 794) on nitrating azobenzene are incorrect. The so-called *p*-nitroazobenzene melting at 137° (compare Gerhardt and Laurent, *Annalen*, 1850, 75, 73; Klinger and Zuurdeeg, *Abstr.*, 1890, 761) consists in reality of a mixture of this compound with *p*-nitroazoxybenzene; in the nitration, a considerable quantity of *p*-dinitroazobenzene is also formed. Janovsky's "*o*-nitroazobenzene," melting at 127°, consists of a similar mixture.

The results obtained by Zinin (*Annalen*, 1841, 38, 222) on nitrating azoxybenzene are confirmed; the compound melting at 88.5°, obtained by reducing *o*-nitroazoxybenzene with alcoholic ammonium sulphide (Zinin, *loc. cit.*), is benzeneazonitrosobenzene,  $C_6H_4\langle\begin{smallmatrix} N \\ | \\ NO \end{smallmatrix}\rangle NPh$ , which on reduction with stannous chloride and hydrochloric acid yields benzene- $\psi$ -azimidobenzene,  $C_6H_4\langle\begin{smallmatrix} N \\ | \\ N \end{smallmatrix}\rangle NPh$  (m. p. 109°).

4:4'-Dinitroazobenzene melts at 121—122°. 3:3'-Dinitroazobenzene, prepared by reducing 3:3'-dinitroazoxybenzene (m. p. 146.5°, Klinger and Zuurdeeg, *loc. cit.*; Lobry de Bruyn, *Abstr.*, 1894, i, 573) with alcoholic ammonium sulphide, crystallises from alcohol in reddish needles and melts at 153°; the red oil obtained by Janovsky in the nitration of azobenzene, which was supposed to be dimetanitroazobenzene, is merely a mixture. Janovsky's *o**p*-dinitroazobenzene is also merely the impure 4:4'-dinitro-compound, and the same is true of his *m**p*-dinitroazobenzene (m. p. 205°), obtained by acting with nitric acid on *p*-nitroazobenzene-*p*-sulphonic acid; the "dinitroazobenzene" melting at 180° is in reality impure 4:4'-dinitroazoxybenzene (*infra*). 2:4-Dinitroazobenzene can be prepared from the synthetically obtained 2:4-dinitrohydrazobenzene as stated by Willgerodt and Ferko (*Abstr.*, 1888, 829).

4:4'-Dinitroazoxybenzene, prepared by leaving 4:4'-dinitroazobenzene in contact with fuming nitric acid for half an hour, crystallises from benzene in stout, sulphur-yellow needles and melts at 192°.

All five of Janovsky's so-called trinitroazobenzenes are shown to be mixtures. That melting at 112° is a mixture of trinitroazoxybenzenes; that melting at 170°, obtained by nitrating *p*-nitroazobenzene, consists of a mixture of *o*- and *m*-trinitroazoxybenzene (Klinger and Zuurdeeg), whilst if the nitration is more carefully regulated, 4:4'-dinitroazoxybenzene (m. p. 185°) is principally formed. The trinitroazobenzene (m. p. 124°), obtained from the so-called *m*-dinitroazobenzene, is a mixture of trinitroazoxybenzenes; on nitrating 4:4'-dinitroazobenzene, either 4:4'-dinitroazoxybenzene (m. p. 185°) is obtained, or 2:4:4'-trinitroazoxybenzene (m. p. 135—136°, Klinger and Zuurdeeg), although



Janovsky has stated that under these conditions a trinitroazobenzene melting at  $160^{\circ}$  is formed. The "trinitroazobenzene" melting at  $185^{\circ}$ , obtained by nitrating 4:4'-dinitroazobenzene at a high temperature, is really 4:4'-dinitroazoxybenzene.

On energetically nitrating azobenzene, there is formed in addition to 2:4:2'-trinitroazoxybenzene (m. p.  $192^{\circ}$ ; Klinger and Zuurdeeg, 187—188 $^{\circ}$ ), and 2:4:3'-trinitroazoxybenzene (m. p.  $178^{\circ}$ ), a large proportion of 2:4:4'-trinitroazoxybenzene (m. p.  $135$ — $136^{\circ}$ ).

On reduction with ammonium sulphide, 4:4'-dinitroazobenzene gives rise to 4:4'-dinitrohydrazobenzene (m. p.  $234^{\circ}$ ), not to Janovsky's so-called "azonitrolic" derivative (compare Lermontoff, Abstr., 1872, 503); as this substance dissolves in alkalis yielding blue salts, Willgerodt has assumed (Abstr., 1890, 1116) it to be an "azhydroxyazo-compound,"  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}(\text{OH}) \cdot \text{O}$ . Since, however, undoubted hydrazo-compounds which are soluble in alkali can be obtained by the interaction of phenylhydrazines with dinitrochlorobenzenes, Willgerodt's views must be rejected. The solubility or non-solubility in alkali of nitrohydrazo-compounds appears, indeed, to depend on the relative position of the nitro-groups; thus 2:4:4'-trinitrohydrazobenzene (*infra*) forms intensely blue salts with alkalis, whilst the 2:4:2'-trinitro-compound is insoluble in alkalis, although a blue coloration is produced on adding these to an acetone solution of the compound; 2:4:3'-trinitrohydrazobenzene fails to produce a coloration even in presence of acetone. Moreover, Willgerodt's views as to the conversion of nitrohydrazo-compounds into aznitroso-compounds by loss of water are incorrect; this decomposition is only possible with compounds which contain an ortho-nitro-group, and even with these in only a few cases. Thus although 2:4-dinitrohydrazobenzene in alcoholic solution is, by adding a drop of alkali, converted instantaneously into the compound 
$$\begin{array}{c} \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \\ | \quad | \quad | \\ \text{NO}_2 \cdot \text{C} - \text{CH} \cdot \text{C} \cdot \text{NO} \end{array} \text{NPh, with 2:4:2',}$$
 2:4:3', and 2:4:4'-trinitrohydrazobenzenes no such conversion is possible.

4:4'-Dinitrohydrazobenzene melts and decomposes at  $234^{\circ}$  (compare Janovsky, Willgerodt, *loc. cit.*), and is readily oxidised to the corresponding azo-compound. 2:4-Dinitrohydrazobenzene (Willgerodt, *loc. cit.*) is converted by fuming nitric acid into 2:4:4'-trinitroazoxybenzene (m. p.  $136^{\circ}$ ). 2:4:4'-Trinitrohydrazobenzene, prepared by the interaction of *p*-nitrophenylhydrazine with 1-chloro-2:4-dinitrobenzene, crystallises best from nitrobenzene in reddish-yellow, lustrous needles, and melts at  $212$ — $213^{\circ}$ ; it is readily converted by mercuric oxide in alcoholic or acetone solution into 2:4:4'-trinitroazobenzene, which crystallises from glacial acetic acid in red needles, melts at  $172^{\circ}$ , and by oxidation with chromic acid is converted into Klinger and Zuurdeeg's trinitroazobenzene melting at  $135$ — $136^{\circ}$ , the constitution of which is thus established. 2:4:3'-Trinitrohydrazobenzene, prepared from *m*-nitrophenylhydrazine and 1:chloro-2:4-dinitrobenzene, on oxidation with mercuric oxide, yields 2:4:3'-trinitroazobenzene (m. p.  $172^{\circ}$ ), and with fuming nitric acid gives rise to 2:4:3'-trinitroazoxybenzene (m. p.  $178^{\circ}$ , Klinger and Zuurdeeg). 2:4:2'-Trinitrohydrazobenzene, prepared from *o*-nitrophenylhydrazine and 1:chloro-2:4-di-

nitrobenzene, crystallises from glacial acetic acid in bright yellow needles, melts at  $220^{\circ}$ , and is identical with the compound obtained by Klinger and Zuurdeeg on reducing trinitroazoxybenzene (m. p.  $192^{\circ}$ ), which the latter considered to be the corresponding azo-compound; 2:4:2'-trinitroazobenzene, prepared by its oxidation, and also by reducing the corresponding azoxy-compound with ammonium sulphide, crystallises from alcohol in reddish needles and melts at  $173^{\circ}$ . Contrary to Klinger and Zuurdeeg's statement, the hydrazo-compound melting at  $220^{\circ}$  is readily acted on by fuming nitric acid, and converted into a substance which forms orange-red needles, melts at  $220^{\circ}$ , and is probably 2:4:2':4'-tetranitroazobenzene, although, owing to its explosive nature, it could not be analysed. W. A. D.

**Preparation of Carbazides. Action of Phenolic Carbonates.** By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1899, 129, 1254—1257).—A mixture of hydrazine phenoxide and carbazide is produced by mixing diphenyl carbonate with an aqueous solution of hydrazine. Diphenylcarbazide is obtained in a similar manner from phenylhydrazine and diphenyl carbonate or guaiaacyl carbonate.

*Diphenyldimethylcarbazide*,  $\text{CO}(\text{NH}\cdot\text{NMePh})_2$ , prepared by heating phenylmethylhydrazine with diphenyl carbonate at  $160$ — $170^{\circ}$ , forms colourless needles melting at  $149$ — $150^{\circ}$ .

$\beta\beta$ -Dinaphthylcarbazide is produced in small quantities by treating diphenyl carbonate (1 mol.) with  $\beta$ -naphthylhydrazine (4 mols.) at  $100^{\circ}$ ; the urethane,  $\text{OPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , obtained when a smaller proportion of the hydrazine (2 mols.) is employed, crystallises in pale yellow spangles. G. T. M.

**Formation of Methæmoglobin.** By RICHARD VON ZEYNEK (*Chem. Centr.*, 1899, ii, 483—484; from *Arch. Anat. Phys.*, 1899, 460—490).—Spectrophotometric examination of alkaline solutions of crystallised methæmoglobin shows that this compound is optically well characterised as an individual substance. By the action of potassium ferricyanide on hæmoglobin, oxygen is liberated. The oxyhæmoglobin decomposes into hæmoglobin and oxygen; the place of the oxygen is taken by other elements or groups which confer weak acid properties for the colour of the compound so formed, and the spectrum of its aqueous solution are changed by the action of a small quantity of alkali. Oxygen is also liberated in the formation of methæmoglobin from oxyhæmoglobin by the action of potassium permanganate, but not by the action of sodium nitrite.

E. W. W.

**Amylase.** By PAUL YVON (*Ann. de l'Inst. Pasteur*, 1899, 13, 523—528. Compare Abstr., 1895, i, 692).—By certain modifications in Lintner's method for the preparation of amylase, a better yield is obtained. H. R. LE S.

## Organic Chemistry.

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**Oxidation of Organic Compounds with Alkaline Potassium Permanganate.** By EDUARD DONATH and HUGO DITZ (*J. pr. Chem.*, 1899, [ii], 60, 566—576).—The authors conclude, from Berthelot's thermo-chemical considerations (*Annalen, Supp.*, 6, 187), that oxidations with acid permanganate are less energetic than those with an alkaline solution of the reagent. With concentrated permanganate, in acid solution and at high temperatures, the final products are usually carbon dioxide and water, but with alkaline permanganate the final product is oxalic acid, reactions which are in accord with Berthelot's third thermochemical law.

The authors question Berthelot's statement that formic acid is produced together with oxalic and carbonic acids in the oxidation of acetylene with alkaline permanganate, since this acid is so readily attacked by the alkaline permanganate that it has been recommended as a method for its estimation, and further, since sodium formate is often added to destroy excess of permanganate in oxidation processes.

Propylene, isobutylene, and amylene (Abstr., 1879, 246), ethyl alcohol (*Jahresber.*, 1867, 337), acetone (Abstr., 1899, i, 251), fatty acids (*Zeit. anal. Chem.*, 1886, 25, 588), butyric, lactic, succinic, and tartaric acids, lactose, dextrose, sucrose, all yield oxalic acid. Alkaline permanganate may be employed for estimating glycerol in fats, acetone in wood naphtha, and also for the estimation of lactic acid (Abstr., 1897, ii, 389). Benzene and toluene are not oxidised by alkaline permanganate; dimethylbenzenes, especially *o*-xylene, are readily oxidised, as also are sulphur compounds, such as carbon disulphide and thiophen—in fact, benzene may be readily freed from thiophen by the aid of alkaline permanganate.

J. J. S.

**Products of the Explosion of Acetylene.** By WILLIAM G. MIXTER (*Amer. J. Sci.*, 1900, 9, 1—9).—Acetylene is not completely decomposed into carbon and hydrogen by electric sparks, even when under a pressure of three atmospheres; the decomposition was, perhaps, somewhat more complete in the experiments made by Berthelot and Vieille, who used pressures varying from 5—30 atmospheres.

It is, however, probable that, after decomposition, a certain amount of acetylene is actually regenerated from the carbon and hydrogen. The residual acetylene was estimated by loss in volume after absorption in ammoniacal solution of cuprous chloride. In some experiments, where the gas was not free from nitrogen, traces of hydrocyanic acid were present; the absence of free cyanogen was somewhat doubtful.

L. DE K.

**Action of Copper on Acetylene: Formation of Cuprene, a highly condensed Hydrocarbon.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 130, 250—252. Compare Abstr., 1899, i, 555).—When acetylene is passed over copper heated at 180—250°, a mixture of hydrogen, unaltered acetylene, and volatile

hydrocarbons is produced ; prolonged action causes the copper to swell and become converted into a yellow mass composed of microscopic filaments. This substance, when compressed, resembles tinder ; it consists of a non-volatile hydrocarbon mixed with 1·7 to 3 per cent. of copper, the composition of the compound corresponding with the empirical formula  $C_7H_6$  (compare Alexander, *Abstr.*, 1899, i, 843). The authors suggest the name *cuprene* for this hydrocarbon, on account of the mode of formation. The substance is insoluble in all the ordinary solvents, and is not attacked by sulphuric acid ; with nitric acid, however, it yields nitro-derivatives ; when heated above  $400^\circ$ , it decomposes into a mixture of volatile hydrocarbons, and leaves a residue of carbon ; it burns with a smoky flame, at the same time evolving an aromatic odour.

G. T. M.

**Action of Hydroxylamine on Dehydracetic Acid.** By GAETANO MINUNNI (*Gazzetta*, 1899, 29, [ii], 452—466).—*Dehydracetic acid monoxime*,  $C_8H_5O_3 \cdot N \cdot OH$ , separates from alcohol in microscopic, rhombic laminae, and from benzene in needles ; it is slightly soluble in acetone, acetic acid, or chloroform. It darkens at about  $140^\circ$ , and becomes almost black at  $145^\circ$ , melting and decomposing at  $153$ — $154^\circ$  if heated rapidly, and at  $149\cdot5$ — $150^\circ$  or  $150\cdot5$ — $151^\circ$  with gentle heating. It dissolves readily in solutions of alkali hydroxides or carbonates and in concentrated sulphuric acid. When treated with acetic anhydride, it yields : (1) an *anhydride*,  $C_8H_7O_3N$ , which crystallises from dilute alcohol in long, white, slender needles melting at  $150\cdot5$ — $151^\circ$  ; (2) an isomeric *compound* separating from dilute alcohol in large, flattened needles having a pungent odour and melting at  $124$ — $125^\circ$ .

Benzoyl chloride converts the monoxime into a *compound*,  $C_8H_9O_4N$ , which is isomeric with it, and crystallises from alcohol in flattened, white needles melting at  $190\cdot5$ — $192^\circ$  ; it gives the normal molecular weight in freezing acetic acid. In the presence of pyridine, the action of benzoyl chloride on the monoxime gives rise to the anhydride,  $C_8H_7O_3N$ , melting at  $150\cdot5$ — $151^\circ$  just described.

*Dehydracetic acid dioxime anhydride*,  $C_8H_5O_3N_2$  ( $= C_8H_5O_2(N \cdot OH)_2 - H_2O$ ), separates from aqueous alcohol in long, white, prismatic needles melting at  $167$ — $168^\circ$  if gently heated, or at  $172$ — $173^\circ$  on more rapid heating. After drying in the air and then over sulphuric acid, it has the composition  $C_8H_5O_3N_2 + H_2O$  ; the mol. of water is lost over sulphuric acid in a vacuum.

T. H. P.

**Isopyromucic Acid.** By L. J. SIMON (*Compt. rend.*, 1900, 130, 255—257).—Isopyromucic acid was first isolated by Limpricht in 1873, who found that it accompanied its isomeride, pyromucic acid, in the product of the dry distillation of mucic acid ; its existence was, however, denied by Oliveri and Peratoner (*Abstr.*, 1890, 1242).

The author finds that isopyromucic acid is produced by distilling a mixture of mucic acid and potassium hydrogen sulphate, and fractionating the aqueous distillate under diminished pressure ; the acid passes over at about  $100^\circ$  under 20 mm. pressure, the yield being 20 per cent. of the theoretical. The acid is colourless when pure, and possesses an empyreumatic odour ; it is readily soluble in alcohol, ether,

chloroform, and hot benzene, but dissolves only sparingly in carbon disulphide. When crystallised from water, it contains  $2\text{H}_2\text{O}$  and melts at  $80\text{--}85^\circ$ ; the anhydrous acid is prepared by distillation or by crystallisation from benzene or chloroform, and melts at  $90\text{--}95^\circ$ . Cryoscopic and acidimetric determinations indicate that it has the molecular formula  $\text{C}_5\text{H}_8\text{O}_3$ . Neutral solutions of the acid, or its sodium and lead salts, develop an intense green coloration with ferric chloride, which is distinguishable even when the dilution corresponds with  $1/10,000$ ; the colour is destroyed by acids. The melting point, solubility, and ferric chloride reaction all agree with the properties of the acid as recorded by Limpricht.

G. T. M.

**Acidimetry of Organic Polybasic Acids.** By A. ASTRUC (*Compt. rend.*, 1900, 130, 253—254. Compare this vol., i, 141, 226; ii, 122).—The acidity of all di- and tri-basic organic acids towards phenolphthalein, Poirrier's blue, litmus, and rosolic acid corresponds with the number of carboxyl groups in the molecule. This is equally true whether the compounds are simple normal, or iso-acids, or whether they possess other functions due to the presence of hydroxyl, halogen, or unsaturated radicles.

The influence of these radicles and of the molecular weight on the acidity becomes apparent when methyl-orange is employed as the indicator. The acidity of oxalic, malonic, and succinic acids diminishes as the molecular weight increases; malonic and isosuccinic acid behave as monobasic acids, whilst succinic acid is neutralised by less than a molecular proportion of alkali, and sebacic acid is neutral. The results agree with Massol's thermochemical investigations on the heat of formation of the salts of these acids. The acidity of the phthalic acids, as indicated by methyl-orange, is greatest for the ortho- and least for the para-isomeride.

Maleic, fumaric, and acetylenedicarboxylic acids exhibit greater acidity than succinic acid, their saturated isologue; the two former are neutralised by one mol. of potassium hydroxide, whilst the acetylene derivative requires a greater amount of the alkali. Itaconic, mesaconic, and citraconic acids are monobasic towards methyl-orange and are therefore more acidic than the saturated dicarboxylic acids containing the same number of carbon atoms. Malic acid is monobasic under the same conditions, and tartronic acid requires for neutralisation even a greater proportion of the alkali; tartaric acid also is more acidic than succinic and malonic acids.

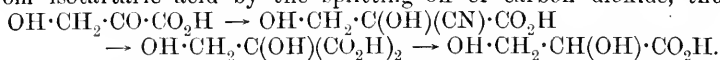
The heat of formation of the salts of these hydroxy-compounds is greater, and the heat of neutralisation of the free acid less, than the corresponding constants of the unsubstituted acids containing the same number of carbon atoms; the acidity, as indicated by methyl-orange, appears therefore to depend on the heat of formation of the salt, and not on the heat of neutralisation of the acid.

Tricarballic and citric acids furnish results in accordance with this generalisation. The presence of a halogen radicle in the molecule increases the acidity of the organic compound; trichloroacetic acid is distinctly monobasic towards methyl-orange, whilst dibromosuccinic acid is dibasic both with this indicator and with phenolphthalein.

G. T. M.

**Optical Activity of Hydroxypyruvic Acid.** By J. H. ABERSON (*Zeit. physikal. Chem.*, 1899, 31, 17—21).—Will's researches (Abstr., 1891, 542) have not decided whether the constitution of this acid is to be represented by  $\text{CHO}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$  or  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ . The former constitution is supported by the fact that a solution of the acid, as obtained by Eder's method, is optically active; it reduces an alkaline silver solution easily, and Fehling's solution on warming; phenylhydrazine gives an osazone melting at  $206-208^\circ$ . Evaporation of this acid solution to dryness (in the course of which traces of oxides of nitrogen may be detected) and subsequent heating in the steam-bath reduces the specific rotation; on repetition of the process, the solution of the acid is no longer optically active, although it behaves in the same way with the reagents named, and an analysis of the calcium salt establishes the composition of the acid; the optical activity observed in the first instance therefore is doubtless due to some impurity containing nitrogen.

By heating the acid in a sealed tube with hydrocyanic acid, and subsequent treatment with hydrochloric acid and baryta, an easily soluble barium salt is obtained, which analysis shows to be barium glycerate; the properties of the free acid are those of glyceric acid, which is formed from isotartaric acid by the splitting off of carbon dioxide, thus:



It follows that hydroxypyruvic acid is a ketonic acid, for if it were an aldehydic acid, ordinary tartaric acid would have been formed, which does not lose carbon dioxide on heating.

J. C. P.

**Solubility in Water of Anhydrides of Organic Acids.** By E. VAN DE STADT (*Zeits. physikal. Chem.*, 1899, 31, 250—254).—The author takes objection to the generally accepted notion that the anhydrides of organic acids are not dissolved by water until converted into the corresponding acids. From the results of time determinations of the solubility of phthalic acid and anhydride, and of succinic acid and anhydride, as well as of mixtures of the corresponding acid and anhydride, it is concluded that the anhydrides are soluble.

T. H. P.

**Acidimetric Value of Substituted Malonic Acids compared with that of Corresponding Normal Dibasic Acids.** By GUSTAVE MASSOL (*Compt. rend.*, 1900, 130, 338—340. Compare Abstr., 1898, ii, 558; 1899, ii, 80, 143, 204, 353, 547).—A review of the author's previous work from which the following general conclusions are drawn:

(1) For normal acids of the oxalic acid series, an increase of  $\text{CH}_2$  produces a decrease in the acidimetric value corresponding with  $2-1$  Cal. Starting from a  $\text{C}_5$  acid, the heat of neutralisation goes on decreasing in value until a minimum is reached, and this takes place when the carboxyl groups are sufficiently distant to exert no influence on each other.

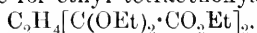
(2) Monosubstituted malonic acids behave like the acids of the oxalic series.

(3) The heat of neutralisation of a normal acid is less than that of a monosubstituted acid containing the same number of carbon atoms and consequently possessing the same molecular weight.

(4) The acidimetric value of dibasic acids depends much more on their structure and on the distance between the carboxyl groups than on their molecular weight.

H. R. LE S.

**Electrolysis of Ethyl Potassium Diethoxysuccinate.** By ALEXANDER CRUM BROWN and HERBERT W. BOLAM (*Proc. Roy. Soc. Edin.*, 1898, 22, 255—257).—Hitherto the method of electrolytic synthesis of dibasic acids has not been found to work where the anion contains a hydroxy- or ethoxy-group; in the case of ethyl potassium diethoxysuccinate, however, the method is applicable. Ethyl diethoxysuccinate was prepared by Purdie's method (*Trans.*, 1885, 47, 856; 1891, 59, 468) and also by the action of sodium ethoxide in alcoholic solution in the cold on ethyl dibromosuccinate; the product thus obtained is the unsymmetrical compound. The ethyl potassium salt, obtained from the ester by the action of alcoholic potash in the cold, was electrolysed (12 volts, 3—4 ampères), and an oil was formed, slightly soluble in water. Analysis of this oil gave numbers agreeing fairly closely with those for ethyl tetraethoxyadipate,



J. C. P.

**Constitution of Saturated Dicarboxylic Acids.** By GUSTAV KOMPPA (*Chem. Centr.*, 1899, ii, 1016—1017; from *Festsch. Polytech. Inst. Finland*).—Undecane- $\alpha\lambda$ -dicarboxylic acid has been prepared from methyl undecenoate,  $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{Me}$ , by treating the hydrogen bromide additive compound,  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_9\cdot\text{CO}_2\text{Me}$ , with ethyl sodiomalonate, and finally removing carbon dioxide from the tricarboxylic acid so formed. This undecanedicarboxylic acid is not identical with brassylic acid obtained from brassidic, erucic, or behenoleic acid, hence all these acids probably contain a side chain. Since Nördlinger's decanedicarboxylic acid, prepared by the action of potassium cyanide on bromoundecioic acid, is the normal acid,  $\text{CO}_2\text{H}\cdot[\text{CH}_2]_{10}\cdot\text{CO}_2\text{H}$ , for it is identical with the acid obtained by the electrolysis of *n*-pimelic acid, it follows that the bromo-compound formed by the combination of hydrogen bromide with methyl undecenoate cannot have the composition  $\text{CO}_2\text{Me}\cdot[\text{CH}_2]_8\cdot\text{CHMeBr}$ . Brassylic acid, prepared by the action of nitric acid on erucic acid, may be purified with great loss by distilling and crystallising the methyl ester; it melts at  $114^\circ$ . The methyl ester melts at  $35^\circ$  and boils at  $326\text{—}328^\circ$ . The amide melts at  $177^\circ$ . Undecane- $\alpha\lambda$ -dicarboxylic acid melts at  $82^\circ$ . The methyl ester is a liquid, and boils at  $319\text{—}321^\circ$ . The amide melts at  $150\cdot5^\circ$ .

Methylundecenoate boils at  $124^\circ$  under 10 mm. pressure. Methyl bromoundecenoate boils at  $165^\circ$  under 10 mm., and at  $158^\circ$  under 6·5 mm. pressure. Methyl undecane- $\alpha\lambda\lambda$ -tricarboxylate,  $\text{CO}_2\text{Me}\cdot[\text{CH}_2]_{10}\cdot\text{CH}(\text{CO}_2\text{Me})_2$ , is an oil, boils at  $223\text{—}224^\circ$  under 10 mm. pressure, and, when hydrolysed, yields an oily acid which is decomposed at  $125^\circ$ , liberating carbon dioxide and forming undecane- $\alpha\lambda$ -dicarboxylic acid,  $\text{C}_{13}\text{H}_{24}\text{O}_4$ . The latter acid separates from benzene as a crystalline powder, crystallises from alcohol in small, colourless needles, and dissolves in 9660 parts of water at  $15^\circ$ , but is much more soluble in organic solvents. The salt,  $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Ag}_2$ ,  $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Ba}$ , forms a white, crystalline powder insoluble in water. The amide,  $\text{C}_{13}\text{H}_{26}\text{O}_2\text{N}_2$ , crystallises from dilute

alcohol in short, colourless needles, and is insoluble in water, but easily soluble in hot alcohol. The *dimethyl* ester,  $C_{15}H_{28}O_4$ , is a rather viscous, colourless liquid, and has a sp. gr. 0.9697 at  $20^{\circ}/20^{\circ}$ .

The electrosynthesis of decanedicarboxylic acid was carried out by Crum Brown and Walker's method. The potassium ethyl salt of *n*-pimelic acid, obtained by partially hydrolysing the diethyl ester with alcoholic potassium hydroxide solution, on electrolysis yields gases which have a melon-like odour, together with an oily mass of diethyl decane-*αα*-dicarboxylate. Decane-*αα*-dicarboxylic acid,  $C_{12}H_{22}O_4$ , crystallises from hot water in slender needles and melts at  $125.5-127^{\circ}$ ; 0.0059 part dissolves in 100 parts of water at  $23^{\circ}$ , and 0.105 in 100 of boiling water. The properties of this acid are identical with those of Nördlinger's acid. E. W. W.

**Synthesis of Campholic Acid by means of Camphoric Acid.** By ALBIN HALLER and G. BLANC (*Compt. rend.*, 1900, 130, 376—378. Compare Abstr., 1896, i, 385 and 448.)—When the campholide obtained by reducing camphoric anhydride with sodium amalgam is dissolved in anhydrous acetic acid and the solution saturated with hydrogen bromide, bromocampholic acid is precipitated in the form of white scales melting at  $177^{\circ}$  and is identical with the acid prepared by Baeyer and Villiger (this vol., i, 133) from the campholide obtained directly from camphor. Bromocampholic acid is converted by heating with zinc dust and acetic acid at  $50-60^{\circ}$  into an acid identical in every respect with campholic acid. The converse transformation of campholic acid into camphor may be effected through camphoric acid, campholide, cyanocampholic acid, and homocamphoric acid. N. L.

**Camphoric Acid.** By LUIGI BALBIANO (*Gazzetta*, 1899, 29, ii, 490—592).—The author brings together and discusses his researches on camphoric acid (compare Abstr., 1893, i, 174; 1894, i, 614; 1895, i, 552; 1897, i, 253; 1899, i, 867). His results are all explainable by Brecht's formula for camphoric acid. T. H. P.

**Camphoric Acid. Synthesis of a Camphor Derivative, 2:3:3-Trimethylcyclopentanone.** By WILLIAM A. NOYES (*Ber.*, 1900, 33, 54—58. Compare Abstr., 1899, i, 284, 759).—A 6 per cent. yield of *ethyl αβ-trimethylbutane-ααδ-tricarboxylate*,



is obtained when the sodium derivative of ethyl methylmalonate is heated with an absolute alcoholic solution of ethyl  $\gamma$ -bromoisohexanoate. It distils at  $170-180^{\circ}$  under 13—15 mm. pressure, and when hydrolysed with alcoholic potash yields the *acid*; this crystallises from ether in needles, melts at  $185-190^{\circ}$ , and at  $190-200^{\circ}$  is converted into  $\alpha\beta$ -trimethyladipic acid. When the latter acid is distilled with lime, it yields the 2:3:3-trimethylcyclopentanone previously obtained from *cis*-campholytic (isolaunonic) acid, the constitution of which

must therefore be  $\begin{array}{c} CMe_2 \cdot CMe \\ | \quad \quad | \\ CH_2 - CH_2 \end{array} > C \cdot CO_2H$  (compare Abstr., 1899, i, 928.) The author considers that this supports Perkin's first con-



stitution for camphoric acid (Proc., 1896, 12, 191) and Bouveault's formula for camphor (*Chem. Zeit.*, 1897, 21, 761). J. J. S.

**Action of Ethyl Iodide on Diethyl Tartrate and Sodium Ethoxide.** By JOHN E. BUCHER (*Amer. Chem. J.*, 1900, 23, 70—82. Compare Michael and Bucher, *Abstr.*, 1896, i, 85, 599, and Lassar-Cohn, *Abstr.*, 1887, 918).—The author has carefully examined the products obtained by acting on ethyl tartrate with ethyl iodide and sodium ethoxide under varying conditions, and has succeeded in proving that, besides the diethyl *as*-diethoxysuccinate shown to be present by Michael and Bucher (*loc. cit.*), some quantity of the *s*-diethoxy-derivative is also produced.

When diethyl tartrate (1 mol.) is boiled with sodium (2 ats.) dissolved in absolute alcohol, a yellowish-brown sodium compound separates, which, on decomposition with acid, yields an oil showing the characteristic reactions of a ketonic ester. On boiling the sodium compound with sodium hydroxide, a considerable quantity of sodium oxalate is obtained. The ketonic ester reacts with phenylhydrazine, and the product, on hydrolysis with alkali, gives a nearly colourless substance having the melting point of 1-phenyl-5-pyrazolone-3-carboxylic acid, and with ferric chloride the violet colour characteristic of that substance, but as the crystals of the compound differed in appearance from those prepared by other methods, the identity of the substance cannot as yet be regarded as established. A. L.

**Malates and Tartromalates.** By CHARLES ORDONNEAU (*Bull. Soc. Chim.*, 1900, [iii], 23, 9—15).—*Calcium α-tartromalate*,  $C_4H_4O_6Ca + C_4H_4O_5Ca$ , obtained by extracting crude calcium tartrate with boiling water, or by adding calcium acetate and excess of ammonia to a mixture of equal weights of malic and tartaric acids, crystallises in microscopic, silky needles containing 9—10H<sub>2</sub>O at the ordinary temperature, and 6H<sub>2</sub>O when dried at 100°. 100 c.c. of water at 20° dissolve 0.27 gram of the salt, which is decomposed by boiling water and by dilute acetic and hydrochloric acids.

*Calcium α-malate* is prepared by boiling crude calcium tartrate with a solution of tartaric acid, adding excess of lime, filtering from the precipitated calcium tartrate, tannin, &c., and evaporating the filtrate. The crystals contain 2H<sub>2</sub>O at 100°; 100 c.c. of water dissolve 0.96 gram at 20° and 0.68 gram at 100°.

*α-Tartromalic acid* is obtained in crystals of the composition  $C_4H_6O_6 + C_4H_6O_5$  by dissolving tartaric acid in excess of a hot, saturated solution of malic acid, or by boiling calcium α-malate with tartaric acid, filtering, and evaporating. When mixed with calcium acetate solution, it yields a precipitate of calcium tartrate, but if the acid is previously neutralised with ammonia, calcium α-tartromalate is formed.

*Calcium hydrogen malate*,  $(C_4H_5O_5)_2Ca + 3H_2O$ , is obtained by treating crude calcium tartrate or calcium malate with the calculated amount of dilute sulphuric acid; the crystals lose 2H<sub>2</sub>O at 100°. 100 grams of water dissolve 2.93 grams of the salt at 20°; the concentrated solution is partially decomposed by boiling, and calcium

$\beta$ -malate is precipitated, but when lime is added to a boiling solution calcium  $\alpha$ -malate is formed.

*Calcium  $\beta$ -malate* is best prepared by boiling calcium hydrogen malate with an equal weight of water; at  $80^\circ$ , a clear solution is obtained, but above that temperature precipitation occurs. Calcium  $\beta$  malate crystallises with  $2\text{H}_2\text{O}$  and is converted by dilute sulphuric acid into ordinary calcium hydrogen malate; when dissolved in hydrochloric acid and saturated with ammonia, crystals of calcium  $\alpha$ -malate slowly separate.

*Calcium  $\beta$ -tartromalate*, prepared by adding calcium acetate to a solution in dilute hydrochloric acid of equal weights of calcium tartrate and  $\beta$ -malate, has the same formula as the corresponding  $\alpha$ -salt, but crystallises in rhombic plates; the crystals contain  $6\text{H}_2\text{O}$  at  $100^\circ$ .

*$\beta$ -Tartromalic acid*, a stable, crystalline compound, is extracted from certain manufactory residues. The calcium hydrogen malate obtained from this acid, after elimination of the tartaric acid by means of potash, reacts with tartaric acid to form calcium  $\alpha$ -tartromalate. N. L.

**Oxidation of Citric and Malic Acids by Potassium Permanganate.** By GEORGES DENIGÈS (*Compt. rend.*, 1900, 130, 32—35).—Citric acid in aqueous solution is oxidised by potassium permanganate at the ordinary temperature with production of carbon dioxide and acetonedicarboxylic acid, which can be isolated by precipitation with mercuric sulphate. A small quantity of oxalic acid is also formed.

If the permanganate is carefully added to a hot solution of malic acid, excess being avoided, there is no liberation of carbon dioxide and oxalacetic acid is formed; this can be precipitated by mercuric acetate solution, which has no effect on malic acid.

In both cases, the permanganate attacks the alcoholic group of the acid, with production of a complex ketone. C. H. B.

**Phenylhydrazine Derivatives of Glycuronic Acid.** By PAUL MAYER (*Zeit. physiol. Chem.*, 1900, 29, 59—69. Compare Thierfelder, 1887, 235, 717; 1889, 378; Hirschl, 1890, 835).—Glycuronic acid, obtained from Indian yellow by Mann and Tollens' method (*Abstr.*, 1896, i, 417), has been treated with 1, 2, 3, and 4 mols. of phenylhydrazine in acetic acid solution. In all cases, a certain amount of tarry matter is produced, but with 1 mol. a compound crystallising in small needles and melting at  $210$ — $217^\circ$  is formed. Its composition agrees with that of glucosazone. When an excess of phenylhydrazine is employed, a compound melting at  $159$ — $164^\circ$  is obtained; although the melting point of this compound is identical with that of pentosazone, it is not a pentosazone, as it contains 11.5, instead of 17.07, per cent. of nitrogen.

From these facts, it follows that phenylhydrazine is of no use as a reagent for glycuronic acid. Bromophenylhydrazine, on the other hand, yields an extremely characteristic compound with glycuronic acid (*Abstr.*, 1899, i, 933), and is probably the best reagent to employ for the detection of the acid. J. J. S.

**Formaldehyde- or Methylene-derivatives of Acids belonging to the Sugar Group.** By G. H. A. CLOWES and BERNHARD TOLLENS (*Annalen*, 1899, 310, 164—189. Compare Weber and Tollens, *Abstr.*, 1898, i, 60).—In preparing monobasic acids of the sugar group by oxidising a glucose with bromine, it is better to add the calcium carbonate before the halogen, instead of afterwards; the lactone hydrate of galactonic acid, prepared by this method, melts at 66°, and has  $[\alpha]_D -67.9^\circ$  (compare Schnelle and Tollens, *Abstr.*, 1892, 1432).

*Dimethylenegalactonic acid*,  $C_6H_8(CH_2)_2O_7$ , prepared from galactonic acid and formaldehyde under the influence of hydrochloric acid, separates from acetone in crystals melting at 136°, and containing  $2H_2O$  or  $1H_2O$ , according as the substance is dried in air or at 40°; it dissolves in 112 parts of water, and a 0.64 per cent. solution has the specific rotatory power  $[\alpha]_D +45.3^\circ$ . The *potassium* and *sodium* salts contain  $1H_2O$ , and the *zinc*, *strontium*, and *copper* salts crystallise with  $2H_2O$ ; the *phenylhydrazine* salt crystallises in needles, and melts at 208°.

*Methylene-d-mannonic lactone*,  $C_6H_8O_6 \cdot CH_2$ , obtained from mannonic acid and formaldehyde, crystallises from acetone and melts at 206°; a 1 per cent. solution has  $[\alpha]_D +91^\circ$ . *Methylene-l-mannonic lactone*,  $C_6H_8O_6 \cdot CH_2$ , melts at 205—207°, and has  $[\alpha]_D -88^\circ$ .

*Xylonic lactone*,  $C_5H_8O_5$ , produced on evaporating an aqueous solution of xylonic acid, crystallises from acetone and melts at 90—92°; a 0.8 per cent. solution has  $[\alpha]_D +74.4^\circ$ . *Dimethylenexylonic acid*,  $C_5H_8(CH_2)_2O_6$ , obtained from calcium xylonate, formaldehyde, and hydrochloric acid, melts at 209—212°, and sublimes without appearing to change; it separates from water with  $\frac{1}{2}H_2O$ , and a 7.5 per cent. solution has  $[\alpha]_D +39.5^\circ$ . The *zinc* and *calcium* salts contain  $3\frac{1}{2}H_2O$  and  $4H_2O$  respectively, and the *phenylhydrazine* salt is stable in air, but decomposes when gently heated.

Arabonic acid has no great tendency to form a methylene derivative, and it is doubtful whether it combines with formaldehyde.

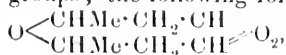
The paper concludes with a complete list of methylene derivatives from acids of the sugar group, and a theoretical discussion by one of the authors (Tollens) relative to the manner in which the methylene group enters the molecule of a polyhydric alcohol or acid, and the position which it occupies.

M. O. F.

**Action of Potassium Cyanide on Aliphatic Aldehydes. II.** By LEOPOLD KOHN (*Monatsh.*, 1899, 20, 903—908. Compare *Abstr.*, 1899, i, 328).—Potassium cyanide reacts vigorously with a solution of formaldehyde. If the temperature of the mixture is not allowed to rise above 30°, hexamethylenetetramine and potassium glycollate are formed.

R. H. P.

**Isodialdane.** By CORNELIS G. LOBRY DE BRUYN and H. C. BIJL (*Proc. K. Akad. Wetensch. Amsterdam*, 2, 143—146).—Isodialdane, obtained by the condensation of aldol in the presence of hydrogen cyanide (Wurtz, *Bull. Soc. Chim.*, 1884, 42, 161), contains neither hydroxyl nor carbonyl groups; the following formula,



best expresses its constitution. This system is very stable, except under the action of dilute acids. There is some analogy between this compound and cane sugar, and the authors propose a formula for the latter, having a similar configuration. G. T. M.

**Condensation of Glyoxal and Isobutaldehyde.** By ERICH VON HORNBOSTEL and EDUARD O. SIEBNER (*Monatsh.*, 1899, 20, 835—836. Compare Abstr., 1896, i, 403).—When glyoxal (1 mol.) and isobutaldehyde (2 mols.), dissolved in alcohol, are condensed by the action of potassium carbonate in strong, aqueous solution and the mixture is distilled, two fractions with the composition  $C_{10}H_{18}O_4$  are obtained. The first distils at  $110^\circ$  under 21 mm. pressure and has a vapour density corresponding with the molecular weight 202; the second is crystalline, melts at  $54^\circ$ , boils at  $139^\circ$ , and has a vapour density corresponding at first with the molecular weight 404, but after longer heating with 202. Under suitable conditions, both fractions appear to change, each into the other. Oxidation of this substance with potassium permanganate solution produces dimethylmalonic acid and a small quantity of a ketone, probably diisopropyl ketone. No reaction occurs with hydroxylamine or with phenylhydrazine. On reduction, a colourless, crystalline substance of the empirical composition,  $C_{10}H_{19}O_4$ , is obtained, which melts at  $123$ — $124^\circ$ , and boils at  $184^\circ$  under 16 mm. pressure; this is also formed when glyoxal and isobutaldehyde are condensed with alcoholic potash.

The compound  $C_{10}H_{18}O_4$  energetically reduces ammoniacal silver solution, whilst the reduction product,  $C_{10}H_{19}O_4$ , has only slight action on it. Both fail to absorb bromine. R. L. J.

**Action of Caro's Reagent on Ketones.** By ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 124—126).—If hydrogen peroxide is mixed with five times its volume of concentrated sulphuric acid, a reagent is obtained, which has an action on ketones such as acetone and tetrahydrocarvone, similar to that of Caro's reagent (see this vol., i, 133). When diluted with water, the reagent at once precipitates iodine from potassium iodide, whilst a mixture of hydrogen peroxide with dilute sulphuric acid does not do this; the authors therefore conclude that the liquid contains an acid analogous to 'chamber crystals,' to which they give the name of 'Caro's acid.'

By the action of Caro's reagent on diethyl ketone, an explosive oil is obtained, which has a pungent odour, immediately liberates iodine from potassium iodide, and is regarded as a simple *diethyl ketone peroxide*,  $CO_2Et_2$ ; if allowed to remain longer in contact with the reagent, or if distilled under the ordinary pressure, it is converted into an oily *polymeride*, which has an ethereal smell and is indifferent to potassium iodide. Dipropyl ketone behaves similarly, and it is supposed that, in the case of acetone also, the first product is an active peroxide which subsequently polymerises. All the polymeric peroxides are decomposed by sulphuric acid, giving rise to the simple peroxides, the formation of which is indicated by their irritating odour and action on potassium iodide paper. T. M. L.

**Isobutylidene-acetone and its Derivatives.** By ADOLF FRANKE and LEOPOLD KOHN (*Monatsh.*, 1899, 20, 876—902. Compare Abstr., 1899, i, 10).—The condensation of isobutaldehyde and acetone belongs

to the class of "aldol" condensations, in which the oxygen atom of the aldehyde is eliminated as water. The resulting compound, *isobutylideneacetone*,  $\text{CHMe}_2 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$ , is a colourless, repulsive smelling liquid, which boils at  $157^\circ$  (corr.) under 750 mm. pressure and at  $51^\circ$  under 16 mm. pressure. In common with most condensation products of aldehydes or aldehydes and ketones, it gives low results on combustion. It yields an unstable *dibromo*-derivative,  $\text{C}_7\text{H}_{12}\text{OBr}_2$ , and on treatment with bromine and dilute potash yields  $\alpha\beta$ -isohexenoic acid (Abstr., 1896, i, 595). On oxidation with cold 1 per cent. solution of potassium permanganate, it yields isopropylglyoxylic acid. The *oxime* boils at  $103^\circ$  under 15 mm. pressure, and on treatment with acetic anhydride yields an *acetyl* derivative, which is a colourless liquid boiling at  $132^\circ$  under 16 mm. pressure, and on further treatment with acetic anhydride yields a crystalline compound melting at  $84^\circ$ .

*Isobutyralacetone* ( $\beta$ -methylhexane- $\gamma$ -ol- $\epsilon$ -one),



obtained as an intermediate product in the above condensation, or when isobutaldehyde and acetone are allowed to remain over a concentrated solution of potassium carbonate, is an oily, viscous liquid, which boils at  $90^\circ$  under 16 mm. pressure, and is easily converted into isobutylideneacetone; it yields an *oxime*, which is a thick, yellowish oil boiling at  $126$ — $129^\circ$  under 16 mm. pressure.

R. H. P.

**Arabinose, Xylose, and Fucose from Tragacanth.** By JOHN A. WIDSTOE and BERNHARD TOLLENS (*Ber.*, 1900, 33, 132—143).—Three samples of white tragacanth, when hydrolysed, yielded fucose and arabinose, whilst fucose and xylose were obtained from two samples of brown tragacanth. Determinations of the specific rotation of fucose derived from tragacanth and from *Fucus* (Tollens, Günther, and Chalmot, Abstr., 1892, 1352) gave values of  $[\alpha]_D$  varying from  $-72^\circ$  to  $-74.5^\circ$ .

R. H. P.

**Complete Synthesis of the Phorone derived from Camphoric Acid.** By LOUIS BOUYEAULT (*Compt. rend.*, 1900, 130, 415—417).—The action of  $\alpha$ -methylecyclopentanone (this vol., i, 171) on acetone in the presence of sodium ethoxide results in the formation of

phorone,  $\text{CMe}_2 \cdot \text{C} \begin{array}{l} \text{CO} - \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , which was identified with the pro-

duct described by Koenigs and Eppens (Abstr., 1892, 626; 1893, i, 361), both by its physical properties and by the preparation of its *oxime* and tribromo-derivative. The former crystallises in slender needles, sublimes very quickly on heating, and melts at  $117^\circ$  in a capillary tube and at  $125^\circ$  on mercury (Koenigs and Eppens give  $121^\circ$ ); it has the composition  $\text{C}_9\text{H}_{13}\text{N} \cdot \text{OH} + \text{H}_2\text{O}$ , as pointed out by Kerp (Abstr., 1896, i, 446), and the presence of the mol. of water indicates that the ethylenic linking in phorone is in the  $\alpha$ -position with respect to the carbonyl group. The tribromo-derivative melts at  $48^\circ$  (Koenigs and Eppens give  $49$ — $52^\circ$ ) and has the composition  $\text{C}_9\text{H}_{13}\text{OBr}_3$ , and not  $\text{C}_9\text{H}_{11}\text{OBr}_3$ .

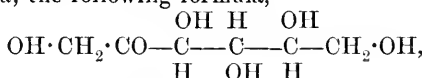
N. L.

**The Resolution of Racemic Compounds into Active Components.** By WILHELM MARCKWALD and ALEX. MCKENZIE (*Ber.*, 1900, 33, 208—210. Compare Abstr., 1899, ii, 733).—In reply to the

criticism of E. Fischer (this vol., i, 140), the authors maintain their claim to the novelty of the method employed by them for the resolution of racemic compounds.

A. H.

*d*-Sorbinose and *l*-Sorbinose ( $\psi$ -Tagatose) and their Configurations. By C. A. LOBRY DE BRUYN and WILLIAM ALBERDA VAN EKENSTEIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 268—271).—The ketose  $\psi$ -tagatose, obtained by the action of alkalis on galactose, is shown to be *l*-sorbinose. It is purified from *d*-tagatose by conversion into its anilide; when pure, it has  $\alpha_D$  42.3°, whilst that of its antipode is -42.7°; their solutions exhibit a slight birotation. The two ketoses are crystallographically identical, and have the same melting point, specific gravity, and solubility in water and the alcohols; when mixed in equal proportion, they yield a well-crystallised racemic compound; their osazones have the same melting point, 150—151°, and *l*-sorbinosazone is identical with *l*-gulosazone. On reduction with sodium amalgam, *d*-sorbinose yields *d*-sorbitol and *d*-iditol, whilst the corresponding alcohols of the *l*-series are obtained from *l*-sorbinose. From these data, the following formula,



has been deduced for *l*-sorbinose.

G. T. M.

Inverting Power of Tartaric, Citric and Oxalic Acids on Sucrose. By H. GILLOT (*Exper. Stat. Record*, 1899, 11, 20; from *Bul. Assoc. Belge Chim.*, 1899, 13, 80—94 and 119—130).—Tartaric acid has a greater inverting power than citric acid, and oxalic acid a greater power than either. The amount of sugar inverted increases considerably with the temperature, amount of acid, and concentration of the solution.

N. H. J. M.

Arabic Acid from Beetroot. By EMIL VOTOČEK and J. ŠEBOR (*Chem. Centr.*, 1899, ii, 1022—1023; from *Zeits. Zuck.-Ind. Böhm.*, 24, 1—15).—Arabic acid, prepared by boiling beetroot pulp with alkalis, is not a homogeneous compound, but is a mixture of neutral substances. The preparations from different materials have different rotatory powers, and also yield varying amounts of arabinose and galactose. Moreover, by hydrolysing the acetyl derivatives of the acid, the original acid is not regained, but the products formed have a greater laevorotatory power and contain different proportions of the groups which yield arabinose and galactose. The salts of arabic acid are to be regarded as alcoholates. Whilst lactobionic acid and maltobionic acid, &c., on hydrolysis yield large quantities of a hexonic acid and hexose, arabic acid, under similar conditions, does not form acid products, but only dextrorotatory substances which are insoluble in alcohol; arabinose and  $\alpha$ -glucose were detected. The three constituents of arabic acid, araban, galactan and glucosan, may not be separate components of the acid, but may possibly form mixed complexes.

The rotatory power of arabic acid is only very slightly increased by lead acetate.

E. W. W.

**Caramel Substances.** By F. STOLLE (*Chem. Centr.*, 1899, ii, 1021—1022; from *Zeit. Ver. Rübenzuck.-Ind.*, 1899, 800—807).—Caramel,  $C_{12}H_{18}O_9$ , prepared by heating the best refined sugar at 180—190°, and removing the undecomposed sugar by fermentation with yeast, is a reddish-brown, amorphous mass, has a conchoidal fracture, is easily soluble in water and melts at 134—136°. It is formed from sugar by the elimination of  $2H_2O$ , and is thus identical with Gélis's caramelan. By treating a concentrated solution of caramelan with ammoniacal lead acetate as long as a precipitate is formed, a compound,  $C_{12}H_{16}O_9Pb$ , is obtained. *Tetracetylcaramelan*,  $C_{12}H_{14}Ac_4O_9$ , prepared by the action of sodium acetate and acetic anhydride, is a dirty brown powder, and is insoluble in water, alcohol, or ether. *Benzoylcaramelan*,  $C_{12}H_{17}BzO_7$ , obtained by the action of benzoyl chloride on a strongly alkaline solution of caramelan, separates as a brown, nodular precipitate which is insoluble in light petroleum, alcohol, or ether, but soluble in glacial acetic acid, concentrated hydrochloric acid, or benzene. E. W. W.

**Action of Hydrogen Peroxide on Aliphatic Amines.** By LEONARD MAMLOCK and RICHARD WOLFFENSTEIN (*Ber.*, 1900, 33, 159—161).—The same results as those obtained by the authors on oxidising dipropylamine and tripropylamine with aqueous hydrogen peroxide have already been published by Dunstan and Gouling (*Trans.*, 1899, 75, 1004). The following facts, however, are new.

Dipropylhydroxylamine,  $NPr_2 \cdot OH$  boils at 72—74° under 30 mm. pressure, and solidifies in the receiver to a white, crystalline mass; on reduction with zinc and hydrochloric acid, it yields dipropylamine, and is converted by sulphurous acid into *dipropylsulphanic acid*,  $NPr_2 \cdot SO_3H$ , which separates from benzene and light petroleum in white crystals and melts at 135°.

On being heated, tripropylamine oxide (tripropylloxamine, Dunstan and Gouling, *loc. cit.*) gives rise to dipropylhydroxylamine and propylene, along with tripropylamine; on heating in a vacuum, the first two products only are formed. Since dipropylhydroxylamine is easily reduced to dipropylamine, a simple method is afforded of passing from a tertiary to a secondary amine. W. A. D.

**Ethylenediamine Compounds of Nickel.** By NICOLAI A. KURNAKOFF (*Zeit. anorg. Chem.*, 1900, 22, 466—470).—When ethylenediamine is added to an aqueous solution of nickel chloride, a blue solution is at first obtained which, on the addition of more ethylenediamine becomes violet. The violet solution contains triethylenediamine nickel chloride, already described by Werner (*Abstr.*, 1899, i, 856). The blue solution contains *diethylenediaminenickel chloride*, which cannot be obtained crystalline. The *platinosochloride*, however, crystallises in six-sided, orange-red prisms; the *platinichloride* in small, orange-yellow, quadratic plates. E. C. R.

**Ethylenediamine Compounds of Palladium.** By NICOLAI A. KURNAKOFF and N. J. GWOSDAREFF (*Zeit. anorg. Chem.*, 1899, 22, 384—386).—Potassium palladochloride, when treated with ethylenediamine, yields a rose-coloured precipitate (probably  $PdCl_2 \cdot 2C_2H_5N_2 \cdot PdCl_2$ ) which dissolves in excess of ethylenediamine and is converted into the compound  $PdCl_2 \cdot 2C_2H_5N_2$ , which separates

in colourless, prismatic crystals. This compound, unlike the corresponding platinum compound, when treated with dilute hydrochloric acid loses ethylenediamine, and is converted into the compound  $\text{PdCl}_2 \cdot \text{C}_2\text{N}_2\text{H}_8$ , which crystallises in small, yellow needles, is sparingly soluble in water, and when treated with thiocarbamide yields the compound  $\text{PdCl}_2 \cdot 4\text{CSN}_2\text{H}_4$ . When dissolved in strong hydrochloric acid, it is converted into *ethylenediammonium palladochloride*,  
 $\text{PdCl}_2 \cdot \text{C}_2\text{N}_2\text{H}_{10}\text{Cl}_2$ .

The latter crystallises in large, reddish-brown plates, decomposes when dissolved in water with loss of hydrogen chloride, and can be recrystallised without decomposition from hydrochloric acid. E. C. R.

**Ethyl Bromoaminocrotonate.** By ROBERT BEHREND and HERMANN SCHREIBER (*Ber.*, 1900, **33**, 265—266. Compare Chattaway and Orton, this vol., i, 152).—*Ethyl β-bromoaminocrotonate*, obtained either by mixing ethereal solutions of acetyl bromoamide and ethyl β-aminocrotonate, or by treating the latter with sodium hypobromite, crystallises from light petroleum in thick prisms or in needles; both modifications melt at 72—74°, but in each case, when the determination is repeated, the melting point is found to be 50°; a mixture of the two forms also melts at the lower temperature. The compound liberates iodine from an acidified solution of potassium iodide; this shows that it contains bromine attached to nitrogen. When treated with dilute sulphuric acid, ammonia is eliminated from the molecule, and ethyl α-bromoacetoacetate results. Ethyl β-chloroaminocrotonate (m. p. 53°) is formed by the action of acetylchloroamide or sodium hypochlorite on ethyl β-aminocrotonate. G. T. M.

**α-Dichlorothiopropionamide.** By JULIUS TROEGER and ERICH EWERS (*J. pr. Chem.*, 1899, [ii], **60**, 520—523).—*α-Dichlorothiopropionamide*,  $\text{CMeCl}_2 \cdot \text{CS} \cdot \text{NH}_2$  or  $\text{CMeCl}_2 \cdot \text{C}(\text{SH}) \cdot \text{NH}_2$ , obtained by the action of hydrogen sulphide on an alcoholic solution of α-dichloropropionitrile in presence of a small quantity of ammonia, crystallises in pale yellow plates, melts and decomposes at about 54°, is soluble in alcohol or ether, and is extremely unstable. E. G.

[Nitrosoalkylurethanes]. By JULIUS W. BRÜHL (*Ber.*, 1900, **33**, 122—124).—A reply to Hantzsch in defence of the spectrometric method of determining the constitution of nitrogen compounds. T. M. L.

**Thiocyanocobaltammonium Compounds.** By JAN VON ZAWIDZKI (*Zeit. anorg. Chem.*, 1900, **22**, 422—423).—A thiocyanocobaltamine chloride is obtained by adding ammonium thiocyanate to a solution of cobalt carbonate in hydrochloric acid, and after the addition of ammonia, oxidising the mixture with air. It crystallises in dark green to black needles, is very unstable, gives off ammonia in the air or in solution, being converted into a reddish powder, and when dissolved in acetic acid and treated with hydrochloric acid yields a blue precipitate. Cobalt nitrate and sulphate yield similar crystalline compounds (Werner, this vol., i, 86). E. C. R.

**Condensation Products of Rubeanic Acid [Dithio-oxamide] with Aldehydes and Secondary Bases.** By OTTO WALLACH (*Chem. Centr.*, 1899, ii, 1024—1026; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—When rubeanic acid [dithio-oxamide] (1 mol.) is condensed with aldehydes,  $\text{R} \cdot \text{CHO}$  (2 mols.), and secondary bases,  $\text{NHR}'_2$ ,



compounds of the type  $(\text{CNSH} \cdot \text{CHR} \cdot \text{NR}')_2$  are formed; the products of the reaction yield lead salts, and therefore contain SH groups (Abstr., 1880, 556). Henry found that formaldehyde combines directly with secondary amines, hence the dithio-oxamide is assumed to act on these additive products,  $\text{OH} \cdot \text{CH}_2 \cdot \text{NR}_2$ , in the pseudo-form  $\text{SH} \cdot \text{C}(\text{NH}) \cdot \text{C}(\text{NH}) \cdot \text{SH}$ , forming  $\text{C}_2(\text{N} \cdot \text{CH}_2 \cdot \text{NR}_2)_2(\text{SH})_2$ , with elimination of  $2\text{H}_2\text{O}$ . The products obtained by the combination of aldehydes and primary bases decompose with elimination of water, and the resulting compounds do not react with dithio-oxamide. These condensation products easily decompose into their components, and are only formed under certain conditions. The aldehyde and base are best dissolved in chloroform and the solution then shaken with dithio-oxamide. In some cases, the mixture requires heating on the water-bath.

The compounds  $\text{C}_{14}\text{H}_{26}\text{N}_4\text{S}_2$ ,  $\text{C}_{16}\text{H}_{30}\text{N}_4\text{S}_2$ ,  $\text{C}_{22}\text{H}_{34}\text{N}_4\text{S}_2$ , and  $\text{C}_{26}\text{H}_{34}\text{N}_4\text{S}_2$  are prepared by condensing formaldehyde, acetaldehyde, valeraldehyde, and benzaldehyde respectively with piperidine and dithio-oxamide. The first compound crystallises in yellowish-red needles and melts at  $143^\circ$ ; the second forms needles, is very unstable, and melts at  $90^\circ$ ; the third separates in yellow crystals and melts at  $119^\circ$ , and the fourth forms pale yellow needles and melts at  $110.5^\circ$ . By the action of formaldehyde and benzaldehyde on methylaniline and dithio-oxamide, the compounds  $\text{C}_{18}\text{H}_{22}\text{N}_4\text{S}_2$  and  $\text{C}_{30}\text{H}_{30}\text{N}_4\text{S}_2$  are formed respectively. The former crystallises in long, red needles and melts at  $139^\circ$ , whilst the latter forms pale yellow needles and melts at  $154^\circ$ . The compound  $\text{C}_{20}\text{H}_{26}\text{N}_4\text{S}_2$ , obtained from formaldehyde, ethylaniline, and dithio-oxamide crystallises in large, yellowish-red needles and melts at  $107^\circ$ . The compound  $\text{C}_{32}\text{H}_{34}\text{N}_4\text{S}_2$ , prepared from formaldehyde, dibenzylamine, and dithio-oxamide, forms large needles and melts at  $123^\circ$ .

The products of the condensation of formaldehyde and diethylamine, of valeraldehyde and diethylamine, of formaldehyde and dipropylamine, and of formaldehyde and diamylamine with dithio-oxamide are red oils. Benzaldehyde, diethylamine, and dithio-oxamide form a compound,  $\text{C}_{24}\text{H}_{34}\text{N}_4\text{S}_2$ , which crystallises in small, pale yellow needles and melts at  $165^\circ$ . The compound  $\text{C}_{36}\text{H}_{58}\text{N}_4\text{S}_2$ , prepared from benzaldehyde, diamylamine, and dithio-oxamide, forms yellow crystals and melts at  $160^\circ$ .

The lead compounds are obtained by mixing the alcoholic solution of the compound with an alcoholic solution of lead acetate.

By the condensation of substituted dithio-oxamides with aldehydes and secondary bases, compounds of the type  $\text{C}_2\text{S}_2(\text{NR} \cdot \text{CHR} \cdot \text{NR}')_2$  are formed, and these substances do not yield lead compounds. The compound  $\text{C}_2\text{S}_2(\text{NMe} \cdot \text{CH}_2 \cdot \text{NMePh})_2$ , prepared from dimethyldithio-oxamide, formaldehyde, and methylaniline, crystallises in yellowish-red needles and melts at  $141^\circ$ . The compound  $\text{C}_2\text{S}_2(\text{NMe} \cdot \text{CH}_2 \cdot \text{NEtPh})_2$ , similarly obtained from ethylaniline, separates in large, red plates and melts at  $108^\circ$ . The compound  $\text{C}_2\text{S}_2(\text{NEt} \cdot \text{CH}_2 \cdot \text{NEtPh})_2$ , prepared from diethyldithio-oxamide, formaldehyde, and methylaniline, forms yellow needles and melts at  $134^\circ$ . Dithio-oxamides which contain aromatic groups, such as diphenyldithio-oxamide, do not form condensation products.

**Rhodicyanides.** By ÉMILE LEIDIE (*Compt. rend.*, 1900, 130, 87—90).—Potassium rhodicyanide,  $K_6Rh_2(CN)_{12}$ , is best obtained by first preparing a saturated solution of recently precipitated hydrated rhodium sesquioxide in a 25—30 per cent. solution of potassium hydroxide, diluting with water until a precipitate of the sesquioxide appears, and then pouring the whole into an excess of a 20—25 per cent. solution of hydrocyanic acid. The mixture is allowed to remain for some time out of contact of air, filtered, the filtrate evaporated in a vacuum, and the salt which separates purified by recrystallisation. This compound belongs to the same class as the ferricyanides, cobalticyanides, &c., for (1) not only is it isomorphous with these compounds, but it has the same optical properties, the same crystallographical angles, &c.; (2) it is decomposed by caustic potash, by concentrated hydrochloric acid with evolution of hydrocyanic acid, and by mercuric oxide with formation of potassium hydroxide, mercuric cyanide, and rhodium sesquioxide, and, lastly, with certain metallic salts it gives precipitates which are characteristic of this class of compounds.

H. R. LE S.

**Transformation of Bisisopropylazimethylene [Isobutaldazine] into 4:4-Dimethyl-5-isopropylpyrazoline.** By ADOLF FRANKE (*Monatsh.*, 1899, 20, 847—875. Compare Abstr., 1899, i, 329).—Isobutaldazine is easily prepared by the action of an aqueous solution of hydrazine sulphate (1 mol.) and sodium carbonate (1 mol.) on pure isobutaldehyde (2 mols.). It forms an argentonitrate,  $C_8H_{16}N_2 \cdot AgNO_3$ , which melts and decomposes at about  $115^\circ$ , and also yields an indefinite, white, crystalline substance on treatment with ethyl iodide. On warming with dilute hydrochloric or dilute sulphuric acid, or by the action of concentrated sulphuric acid in the cold, it is decomposed with re-formation of the aldehyde and a hydrazine salt; on treatment, however, with concentrated hydrochloric, fuming hydriodic, or maleic acid (compare Curtius and Zinckeisen, Abstr., 1899, i, 165), it is converted into a salt of 4:4-dimethyl-5-isopropylpyrazoline. 4:4-Dimethyl-5-isopropylpyrazoline, prepared by treating any of its salts with dilute alkalis, is a clear and somewhat viscous oil boiling at  $202.5^\circ$  (corr.), which has a camphor-like odour and is still liquid at  $-20^\circ$ . The hydrochloride, prepared by the action of concentrated hydrochloric acid on isobutaldazine, forms transparent, colourless, monoclinic, holohedral crystals melting at  $149^\circ$ ; its aqueous solution colours woody tissue an intense yellow, but gives no coloration with potassium dichromate and sulphuric acid, thus showing that Knorr's reaction is only given by pyrazolines containing a phenyl group. The hydriodide obtained in the above manner forms colourless crystals. The acetyl derivative,  $C_8H_{15}N_2 \cdot Ac$ , is a thick oil boiling at  $120—125^\circ$  under 19 mm. pressure, and the benzoyl derivative crystallises in the form of small needles melting at  $70^\circ$ . The pyrazoline forms indefinite additive products with ethyl iodide and bromine, but is not attacked by alkaline reducing agents. Oxidation with a very dilute solution of potassium permanganate yields diisopropyl ketone, and an undetermined compound,  $C_8H_{14}ON_2$ , which is a colourless oil boiling at  $245^\circ$ , together with small quantities of oxalic,  $\alpha$ -hydroxyisobutyric, isobutyric, and acetic acids.

*Propionaldazine*,  $N_2(CH_2Et)_3$ , prepared in a similar manner to isobutaldazine, is a clear, mobile liquid boiling at  $144-146^\circ$ . *Capronaldazine* is a clear, viscous oil boiling at  $246^\circ$ . These two aldazines, and the dimethyl- and diethyl-ketazines are decomposed in ethereal solution by dry hydrogen chloride, although propionaldazine yields traces of an oil which has a camphor-like odour and may be a pyrazoline derivative.

R. H. P.

**Action of Mercury on Methylene Iodide.** By VICTOR THOMAS (*Bull. Soc. Chim.*, 1900, [iii], 23, 49—51).—The author confirms Sakurai's statement (*Trans.*, 1880, 37, 658) that the interaction of mercury, methylene iodide, and mercurous iodide in the cold results in the formation of the compound  $CH_2I_2 \cdot Hg$  and other products, but finds that the mercurous iodide plays no part in the reaction, which takes place equally well in the absence of this salt. When mercury is heated with methylene iodide for 10—12 hours in a sealed tube at  $190-200^\circ$ , large crystals of mercuric iodide are formed, and on opening the tube a mixture of methane (1 vol.) and ethane (2 vols.) is liberated.

N. L.

**Secondary Butylbenzene.** By TADEUSZ ESTREICHER (*Ber.*, 1900, 33, 436—443).— $\beta$ -Chlorobutane boils at  $66.5^\circ$  under 731.8 mm. pressure, has a sp. gr. 0.8948 at  $0^\circ$ , and a critical temperature lying between  $246.7^\circ$  and  $248.4^\circ$ . *sec*-Butylbenzene, prepared from benzene, aluminium chloride, and  $\beta$ -chlorobutane or *sec*-butyl chloride, boils at  $173.2-174.2^\circ$  under 742.4 mm. pressure; on treatment with fuming sulphuric acid, it yields *sec-butylbenzene-p-sulphonic acid*; this forms deliquescent crystals melting at  $84-85^\circ$ , yields a *barium* salt crystallising in needles or tablets with  $1\frac{1}{2}H_2O$ , and an easily soluble *potassium* salt crystallising in needles. *p-sec-Butylphenol*, obtained by fusing the sulphonic acid with potash, crystallises in long, silky needles, melts at  $53-54^\circ$ , and boils at  $239.5-240.5^\circ$  under 750.6 mm. pressure; its *acetyl* derivative is a clear liquid with an anise-like odour and boils at  $255.5^\circ$  under 743.9 mm. pressure.

R. H. P.

**Explanation of the Würtz-Fittig Synthesis. IV. Bromomesitylene and Sodium; Mesityl Bromide and Sodium.** By MAX WEILER (*Ber.*, 1900, 33, 334—345. Compare *Abstr.*, 1894, i, 604; 1896, i, 237, 242; 1899, i, 490).—Mesitylene has been employed as a diluent instead of ether or benzene in the reaction between bromomesitylene and sodium with the result that a yield of 14.2 instead of 8.9 per cent. of hydrocarbons containing two mesityl groups has been obtained. This mixture may be separated into 40.8 per cent. of *s*-tetramethyldibenzyl (m. p.  $78^\circ$ ), 9.7 per cent. of 3:5:2':4':6'-pentamethyldiphenylmethane (*Abstr.*, 1899, i, 703), 12.6 per cent. of a crystalline mixture of the above, and 29.4 per cent. of a yellow, non-crystallisable oil with a purple fluorescence. Practically the same products are obtained when mesityl bromide is treated with sodium in the presence of mesitylene.

The interpretation previously given is held to cover these new facts, as also that given by Nef (*Annalen*, 1887, 298, 372; 1899, 309, 167). *s*-Tetramethyldibenzyl, the so-called dimesityl (*loc. cit.*), has also been obtained by Moritz and Wolfenstein (*Abstr.*, 1899, i, 910) by the

action of persulphates on mesitylene. On oxidation with chromium trioxide, it does not yield any definite products; with nitric acid, it gives a small amount of mesitylenic acid, and with potassium permanganate trimesic acid. Its constitution follows from the following method of synthesis. *s*-Tetramethylbenzoin is readily obtained by the action of alcoholic potassium cyanide on *s*-dimethylbenzaldehyde; it crystallises in long, yellow plates melting at 93—94°, dissolves readily in most organic solvents, reduces Fehling's solution in the cold, gives a red coloration with ferric chloride and when reduced with hydriodic acid and phosphorus yields *s*-tetramethyldibenzyl together with a substance melting at 72—75°.

When pentamethyldiphenylmethane is brominated in the presence of iodine, it yields a *tetrabromo*-derivative,  $C_{18}H_{18}Br_4$ , which crystallises from benzene in plates or stout needles melting at 230—232°, and is not decomposed when boiled for 1½ hours with alcoholic potash. When oxidised with chromium trioxide, the hydrocarbon yields a small amount of an acid together with a substance which crystallises in yellow needles, melts at 229—232°, and is probably 1:3:5:7-tetramethylantraquinone. When alkaline permanganate is employed, an acid is obtained which crystallises from hot water in small prisms, sinters at 350—355°, and yields a methyl ester melting at 146—147°. When treated in carbon disulphide solution with chromyl chloride, the hydrocarbon yields a certain amount of mesitoylmesitylene together with other products. Mesitoylmesitylene (Abstr., 1899, i, 704), when treated with zinc and aqueous alcoholic potash by Elbs's method (Abstr., 1886, 461), yields *pentamethylbenzhydrol*, which crystallises in long, stout prisms, melts at 98—99°, and is readily soluble in most organic solvents. It does not react with sodium hydroxide and benzoyl chloride, or with acetic anhydride or phenylcarbimide in the cold; on boiling, the *acetate* melting at 111·5—112, is formed. When reduced with hydriodic acid and phosphorus, it yields pentamethyldiphenylmethane.

J. J. S.

**Acetylation with Acetic Anhydride in Aqueous Solution.** By JOHANNES PINNOW (*Ber.*, 1900, 33, 417—420).—It is shown that the acetates of aromatic amines in aqueous solution or suspension can be directly acetylated if placed in contact with acetic anhydride. Quantitative experiments with 1 per cent. aniline acetate solutions show that, at any temperature between 20° and 50°, 99 per cent. of the acetic anhydride is converted into acetanilide. An aqueous solution of aniline hydrochloride can be thus acetylated despite the free hydrochloric acid, and even when the latter is considerably in excess (1 mol. aniline to 4 mols. HCl) about 15 per cent. of the anhydride is converted into acetanilide.

R. H. P.

**[Acylation] in Presence of Pyridine.** By GAETANO MINUNNI (*Gazzetta*, 1899, 29, ii, 443—451).—A historical review of researches on the acetylation and benzylation of hydroxy-, amino-, and imino-compounds in presence of pyridine.

T. H. P.

**Nitration of Dimethylaniline dissolved in Concentrated Sulphuric Acid.** By PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 342—344).—When dimethylaniline

dissolved in concentrated sulphuric acid is treated with excess of nitric acid, the chief products of reaction are the *m*- and *p*-mononitro-compounds, a small amount of 2:4-dinitrodimethylaniline being simultaneously formed. If the solution be added to a mixture of ice and water, further nitration occurs and the two dinitro-compounds previously described by the author are produced; mononitro-compounds only are obtained when the dilution is effected in the presence of excess of caustic soda. This result is confirmed by direct experiment, the two dinitro-compounds being prepared by nitrating *m*-nitrodimethylaniline in 30 per cent. sulphuric acid. It is probable that, by nitrating dimethylaniline by Groll's method, the meta-compound is exclusively formed in the concentrated sulphuric acid, whilst the para-isomeride is produced after dilution. 2:4-Dinitrodimethylaniline is the sole product of the nitration of *p*-nitrodimethylaniline.

G. T. M.

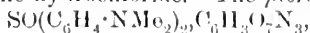
**Action of Thionyl Chloride on Dimethylaniline and Diethylaniline.** By AUGUST MICHAELIS and P. SCHINDLER (*Annalen*, 1899, 310, 137—155. Compare Abstr., 1893, i, 515).—It has been shown by Michaelis and Godchaux that, when thionyl chloride acts on dimethylaniline dissolved in a small quantity of ether, thiodimethylaniline and dimethylanilinesulphonic chloride are produced.

The compound  $2\text{NMe}_2\text{Ph}\cdot\text{SOCl}_2$ , obtained on adding thionyl chloride, diluted largely with light petroleum, to a very dilute, ice-cold solution of dimethylaniline (1 mol.) in the same medium, forms dark red, hygroscopic crystals, which become yellow and resinous when exposed to moist air; the colour changes to green at  $80^\circ$ , and the substance melts at  $100^\circ$ . Cold water resolves this compound into dimethylaniline, thiodimethylaniline, sulphur dioxide, a yellow powder of uncertain character having the composition  $\text{NMe}_2\text{Ph}\cdot\text{SO}_2$ , and dimethylanilinesulphinic acid,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$ , of which the sodium salt crystallises in long needles, and the potassium salt in large, rhombic plates.

*Dimethylaminophenylethylsulphone*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Et}$ , prepared from sodium dimethylanilinesulphinate and ethyl bromide, crystallises from water in lustrous leaflets and melts at  $116^\circ$ ; the hydrochloride melts at  $139$ — $140^\circ$ .

*Dimethylaminophenylmethylsulphone*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Me}$ , crystallises from hot water in colourless needles and melts at  $166$ — $167^\circ$ .

*Thionyl dimethylaniline*,  $\text{SO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , produced by the action of acids on the salts of dimethylanilinesulphinic acid, separates from water in lustrous crystals and melts at  $151$ — $152^\circ$ , forming a dark blue liquid; hydrochloric acid resolves it into dimethylaniline and sulphur dioxide, whilst sodium reduces the alcoholic solution to thiodimethylaniline. The hydrochloride melts at  $174^\circ$ , and in neutral solution yields the *platinichloride* containing  $8\text{H}_2\text{O}$ , which decomposes at  $50^\circ$  without melting; the *platinichloride* containing  $2\text{H}_2\text{O}$  is obtained on adding platinic chloride to a strongly acid solution of thionyl dimethylaniline hydrochloride. The *picrate*,



melts at  $119^{\circ}$ , and the *picrate*,  $\text{SO}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises from hot water in slender needles and melts at  $155-156^{\circ}$ .

The compound  $2\text{NEt}_2\text{Ph} \cdot \text{SOCl}_2$ , prepared from diethylaniline and thionyl chloride, forms red crystals, and is converted by water into diethylanilinesulphinic acid, the *sodium* and *potassium* salts of which form lustrous, colourless crystals.

*Thionyldiethylaniline*,  $\text{SO}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$ , obtained by the action of boiling water on diethylanilinesulphinic acid, forms small, lustrous crystals, and melts at  $128-129^{\circ}$ ; it yields two *platinichlorides*, containing  $8\text{H}_2\text{O}$  and  $2\text{H}_2\text{O}$  respectively. M. O. F.

**Stereochemical Observations on the Reaction between Picric Chloride and Aromatic Amines.** By EDGAR WEDEKIND (*Ber.*, 1900, 33, 426—436. Compare Turpin, *Trans.*, 1891, 59, 714).—It has been shown by Wedekind and Stauwe (*Abstr.*, 1898, i, 192, 573), in studying the influence of the relative positions of substituents on the formation of tetrazolium bases, that the nitro-group forms an exception to the known rules, and therefore the action of picryl chloride on various amines has been studied. Of the various monosubstituted primary amines, the *para*-compounds form the picryl derivatives most readily, followed by the *meta*-, and then the *ortho*-compounds, although there is not much difference between them. The nitro group again forms an exception, since, for example, *m*-nitraniline forms a picryl derivative with the greatest ease, and *o*-nitraniline only with great difficulty. The stereochemical influence of the *ortho*-position is strikingly shown by the picrylaminoacetophenones, of which the *para*-compound easily forms a phenylhydrazone, whilst the *ortho*-compound will not react with phenylhydrazine.

Secondary amines of the type  $\text{NHXY}$  (where  $\text{X} = \text{Ph}$ ,  $\text{Y} = \text{Me}$ ,  $\text{Et}$ ,  $\text{CH}_2\text{Ph}$ ) or piperidine form normal picryl derivatives; diphenylamine and carbazole, on the other hand, form additive compounds with 2 mols. of picryl chloride, this being probably the first stage of the reaction, of which the completion is hindered by stereochemical causes. Compounds of the phenylenediamine type (even *para*-compounds) form only monopicryl derivatives, whilst those of the benzidine series form dipicryl derivatives, which, curiously, are soluble in alkalis and reprecipitated by acids.

The following picryl derivatives were prepared by treating 2 mols. of the amine with 1 mol. of picryl chloride; the melting points are quoted; the figures in brackets give the yield expressed as percentage of that theoretically possible.

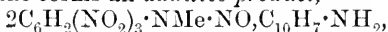
Picrylpiperidine (Turpin, *loc. cit.*),  $104-106^{\circ}$ , (73.5); *o*-picrylamino-benzoic acid,  $271-272^{\circ}$ , (84.7); *m*-picrylamino-benzoic acid,  $233-234$ , (84.7); *p*-picrylamino-benzoic acid,  $292-293^{\circ}$ , (97.9); *o*-picrylnitro-aniline,  $220^{\circ}$ , (5.3); *m*-picrylnitroaniline (Austen, this *Journ.*, 1874, 165),  $202-203^{\circ}$ , (91.2); *p*-picrylnitroaniline (Austen, *loc. cit.*),  $214-215^{\circ}$ , (80.2); *o*-picrylchloroaniline,  $158-159^{\circ}$ , (86); *m*-picrylchloroaniline,  $137-139^{\circ}$ , (88.9); *p*-picrylchloroaniline,  $169-170^{\circ}$ , (92.5); *p*-picrylaminoacetophenone,  $162-163^{\circ}$ , (98.5); *o*-picrylaminoacetophenone,  $232^{\circ}$ ; *o*-picrylamino-benzaldehyde,  $203-205^{\circ}$ ; *p*-picrylamino-phenol (Turpin, *loc.*

*cit.*), 172—173°, (97—98); *m*-picrylamino*phenol*, 203—204°, (86—88); *p*-picrylaminoacetanilide, 240—242°; picrylmethylaniline (Turpin, *loc. cit.*), 108—110°, (65—70); picrylethylaniline, 105—107°, (50—60).

The phenylhydrazone of *p*-picrylaminoacetophenone melts at 218—219°. Diphenylamine forms an additive compound with 2 mols. of picric chloride, which crystallises in lustrous, red tablets melting at 63—64° (compare Turpin, *loc. cit.*). The analogous compound derived from carbazole forms yellowish-red needles melting at 160—165°.

R. II. P.

**Nitrosoamines of Methylated Nitroanilines.** By EUGEN BAMBERGER and JENS MÜLLER (*Ber.*, 1900, 33, 100—113. Compare *Abstr.*, 1897, i, 241).—*Nitrosomethylpicramide*,  $C_6H_2(NO_2)_3 \cdot NMe \cdot NO$ , prepared by the action of nitrous fumes on a solution of methylpicramide, crystallises from alcohol in glistening, yellow, rhombic plates or slender needles, and melts at 106·5°; caustic alkalis, methylamine, and ammonia turn the alcoholic solution to a blood-red colour (compare the 'nitroic acids' of Hantzsch and Kissel, this vol., i, 89); unlike *p*-nitromethylanilinenoitrosoamine, it does not liberate diazomethane when boiled with methyl alcoholic potash, and it also differs from nitrosoacetanilide (*loc. cit.*) in that it does not give any trinitrodiphenyl when boiled for two days with dry benzene. When mixed with  $\alpha$ -naphthylamine in benzene or alcoholic solution, picrylmethylnitrosoamine forms an additive product,



which separates in dark brown to black needles, melts at 120·5—121°, and can be crystallised unchanged from benzene; it is completely dissociated in solution, and the free nitrosoamine can be separated in part by diluting the solution with water; the solution in sulphuric acid is olive-green, but becomes deep red on adding water. When warmed with alcohol, or left in contact with it in the cold for some days, the additive product is converted into picryl- $\alpha$ -naphthylamine, but no diazomethane is produced. The additive product with  $\beta$ -naphthylamine was not separated from the dark brown solution, but was converted directly into picryl- $\beta$ -naphthylamine. This crystallises from acetic acid in glistening, coral-red prisms, with a metallic lustre, and melts at 233—233·5°; it also exists in a second, orange-yellow modification, which melts at the same temperature. Ammonia converts the nitrosoamine into picramide, whilst aniline gives an orange-red picrylaniline, melting at 178—179°, which is probably a second modification of the scarlet-red picrylaniline, melting at 175°, prepared by Clemm from picryl chloride and aniline (*Ber.*, 1870, 3, 126). When heated at 70—80° for several days, the nitrosoamine is partly converted into methylpicramide. The additive product of methylpicramide and  $\beta$ -naphthylamine,  $C_6H_2(NO_2)_3 \cdot NHMe, C_{10}H_7 \cdot NH_2$ , crystallises from alcohol in dark brown needles with a violet shimmer, and melts at 132·5—133°.

An additive product,  $C_6H_2Cl(NO_2)_3, C_{10}H_7 \cdot NH_2$ , separates in brown needles on mixing cold alcoholic solutions of picryl chloride and  $\alpha$ -naphthylamine, sinters at 110·5—111·5°, and melts with decomposition at 180°; under other conditions, picrylnaphthylamine is formed directly,

2 : 4-Dinitrophenylmethylnitrosoamine,  $C_6H_3(NO_2)_2 \cdot NMe \cdot NO$ , crystallises from alcohol in pale yellowish needles, melts at  $83-84.5^\circ$ , and is fairly stable when pure; when boiled with dry benzene, it does not give dinitrodiphenyl, but is partially converted into dinitromethylaniline. By the action of  $\alpha$ -naphthylamine on the nitrosoamine, a mixture of aminoazonaphthalene and dinitromethylaniline is produced.

*p*-Nitrophenylmethylnitrosoamine is not changed by boiling with benzene, and does not convert  $\beta$ -naphthol into the methyl ether; the nitroso-group is very stable, but can be removed by boiling with  $\alpha$ -naphthylamine and fusel oil, giving *p*-nitromethylaniline and (apparently) aminoazonaphthalene.

T. M. L.

Relation of Fulminic to Isocyanic Acid and the Formation of Phenylurethane from Phenol and Mercuric Fulminate. By ROLAND SCHOLL and F. KACER (*Ber.*, 1900, 33, 51-54. Compare Abstr., 1891, 282).—Phenylurethane,  $NH_2 \cdot CO_2Ph$ , is formed when mercuric fulminate is moistened with alcohol and added in small portions to phenol heated at  $150-160^\circ$ .

J. J. S.

The Molecular Rearrangement of *o*-Aminophenyl Ethyl Carbonate to  $\alpha$ -Hydroxyphenylurethane. By JAMES H. RANSOM (*Amer. Chem. J.*, 1900, 23, 1-50. Compare Abstr., 1898, i, 415).—The substance obtained by reducing *o*-nitrophenyl ethyl carbonate with tin and hydrochloric acid (Bender, Abstr., 1887, 37) is Groenvik's *o*-hydroxyphenylurethane,  $OH \cdot C_6H_4 \cdot NH \cdot CO_2Et$  (this Journ., 1877, i, 473), and its formation is therefore due to a migration of the carboxyethyl group; it melts at  $86.5^\circ$ , not  $95^\circ$  as stated by Bender, or  $120^\circ$  by Groenvik.

*o*-Benzoyloxyphenylurethane,  $OBz \cdot C_6H_4 \cdot NH \cdot CO_2Et$ , is insoluble in alkalis or acids, and melts at  $75.5^\circ$ ; when distilled, it yields alcohol, ethyl benzoate, benzoylcarbonylaminophenol, benzenylaminophenol, and a substance melting at  $85-105^\circ$ , probably impure carbonylaminophenol. Benzoylcarbonyl-*o*-aminophenol,  $C_6H_4 \langle \overset{NBz}{O} \rangle CO$ , is also made by treating carbonylaminophenol in alkaline solution with benzoyl chloride; it melts at  $174^\circ$ .

*m*-Nitrobenzoyloxyphenylurethane,  $NO_2 \cdot C_6H_4 \cdot CO_2 \cdot C_6H_4 \cdot NH \cdot CO_2Et$ , is soluble in alcohol, ether, or benzene, insoluble in alkalis and acids, and crystallises from a mixture of benzene and light petroleum in slender prisms melting at  $86.5^\circ$ . On distillation, it yields alcohol, *m*-nitrobenzoic acid and its ethyl ester, carbonylaminophenol, and *m*-nitrobenzenyl-*o*-aminophenol,  $C_6H_4 \langle \overset{N}{O} \rangle C \cdot C_6H_4 \cdot NO_2$ . This substance is also obtained by heating together *o*-aminophenol and *m*-nitrobenzoyl chloride; it is sparingly soluble in the usual organic media excepting chloroform, and separates from alcohol in greyish-yellow crystals melting at  $207^\circ$ .

*m*-Nitrobenzoylcarbonylaminophenol is somewhat soluble in acetic acid, readily soluble in chloroform, and melts at  $199.5-201.5^\circ$ . *m*-Nitrobenzoyl-*o*-aminophenol dissolves in alkalis, forming a bright yellow solution, and crystallises from alcohol in thick prisms melting



at 207°. When treated with ethyl chloroformate and potassium hydroxide, it affords *m*-nitrobenzoylhydroxyphenylurethane.

*m*-Nitrobenzoyl-*o*-aminophenyl benzoate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$ , separates from alcohol in long, white, hair-like needles, is not very soluble in alcohol, and melts at 151—153°. *Benzoyl-o-aminophenyl m-nitrobenzoate*, crystallises in short, thick prisms, and melts at 152°. Both the foregoing substances, on hydrolysis with alkali, yield benzoyl-*o*-aminophenol and *m*-nitrobenzoic acid, but cannot be converted into one another.

*Carbethoxyaminophenyl phenylcarbamate*,

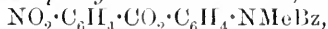
$\text{NHPh} \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , or  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO}_2\text{Et}$ , made by treating a solution of hydroxyphenylurethane and phenylcarbimide in absolute ether with aluminium chloride, separates from alcohol in nearly white prisms melting at 116—118°, and is fairly soluble in most of the ordinary media, but insoluble in alkalis or acids.

When hydroxydiphenylcarbamide in alkaline solution is treated with ethyl chloroformate, an oil is precipitated which, on hydrolysis, yields hydroxyphenylurethane.

*Carbonylmethylaminophenol*,  $\text{C}_6\text{H}_4 \langle \text{NMe} \rangle \text{CO}$ , is very soluble in most organic solvents and melts at 86°. *o*-Methylaminophenol melts at 88—90° (compare Seidel, Abstr., 1891, 53). *Benzoylmethyl-o-aminophenol*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMeBz}$ , melts at 160—162°. *Benzoylmethyl-o-aminophenyl ethyl carbonate* separates from light petroleum in long, silky needles, melts at 68°, and is soluble in alcohol, ether, or benzene; on alkaline hydrolysis, it yields benzoylmethyl-*o*-aminophenol. *o*-Hydroxyphenylmethylurethane,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CO}_2\text{Et}$ , melts at 53°, dissolves in alkalis, and is reprecipitated by acids. *o*-Benzoyloxyphenylmethylurethane,  $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CO}_2\text{Et}$ , crystallises in needles, melts at 88—90°, is fairly soluble in most organic media, but insoluble in alkalis or acids.

*m*-Nitrobenzoylmethyl-*o*-aminophenol,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , separates from alcohol in beautiful, large crystals, melts at 105°, and decomposes at 110—115°; the benzoate,  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$ , melts at 141°.

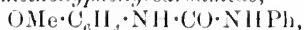
*Benzoylmethyl-o-aminophenyl m-nitrobenzoate*,



separates from alcohol in large, stout crystals melting at 123.5°.

*o*-Methoxyphenylurethane,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , made by the action of ethyl chloroformate on anisidine in presence of alkali, is a nearly colourless oil boiling at 180—182° under 26 mm. pressure; the monobromo-derivative appears to melt at 102.5°, but is mixed with a second substance melting at 252°, from which it is difficult to separate it.

*o*-Methoxyphenylurethane is converted into *o*-methoxyphenylcarbamide (m.p. 146.5°) on treatment with phosphorus pentachloride and ammonia. *Phenyl-o-methoxyphenylcarbamide*,



separates from a mixture of chloroform and light petroleum in thick prisms, melts at 144°, and is soluble in alcohol, ether, or chloroform.

*o*-Hydroxyphenylurethane is easily methylated by von Pechmann's method with diazomethane, yielding *o*-methoxyphenylethylurethane.

*o*-Aminophenyl ethyl carbonate,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO}_2\text{Et}$ , made by reducing *o*-nitrophenyl ethyl carbonate with tin and hydrochloric acid at  $0^\circ$ , forms an oil which, when kept over sulphuric acid, changes to *o*-hydroxyphenylurethane. The *hydrochloride*,  $\text{C}_9\text{H}_{11}\text{ON}_3\text{HCl}$ , is a white solid which melts and evolves gas at  $150$ — $152^\circ$ , and when heated in aqueous solution deposits hydroxyphenylurethane. The *platinichloride*,  $\text{C}_9\text{H}_{11}\text{ON}_3\text{PtCl}_6$ , forms yellow crystals. Attempts to prepare a benzoyl derivative of aminophenyl ethyl carbonate resulted in the formation of the benzoyl derivative of hydroxyphenylurethane.

As it was thought that the hydrochloride of ethoxymethenylaminophenol might be formed during the reduction of *o*-nitrophenyl ethyl carbonate, a comparison of ethoxymethenylaminophenol with aminophenyl ethyl carbonate was made; it was found that on passing hydrogen chloride into its solution in absolute ether or light petroleum, ethyl chloride was evolved and carbonylaminophenol was produced, a fact which indicates that the base is not an intermediate product in the formation of *o*-hydroxyphenylurethane.

*p*-Nitrophenyl ethyl carbonate, made from *p*-nitrophenol or by nitrating phenyl ethyl carbonate, is soluble in light petroleum, ether, or alcohol, and crystallises in long, white needles melting at  $68^\circ$ . *p*-Aminophenyl ethyl carbonate melts at  $36^\circ$ , dissolves in acids, and gives no purple colour with ferric chloride; the *hydrochloride*,  $\text{C}_9\text{H}_{11}\text{ON}_3\text{HCl}$ , darkens at  $160^\circ$  and melts at  $197^\circ$  with violent decomposition; the *platinichloride*,  $(\text{C}_9\text{H}_{11}\text{ON}_3)_2\text{H}_2\text{PtCl}_6$ , is a bright yellow, crystalline solid which blackens at  $208^\circ$  and melts at  $237^\circ$ . *p*-Ureidophenyl ethyl carbonate is insoluble in alkalis and melts at  $147$ — $150^\circ$ . All attempts to cause a rearrangement of the molecule of *p*-aminophenyl ethyl carbonate were unsuccessful. A. L.

**Oxidation of Aqueous Solutions of Aromatic Hydroxylamines by Atmospheric Oxygen.** By EUGEN BAMBERGER (*Ber.*, 1900, 33, 113—122).—The first product of the oxidation of  $\beta$ -phenylhydroxylamine and its substitution products by oxygen in aqueous solution is a nitrosobenzene, which usually combines more or less rapidly with the unchanged phenylhydroxylamine to form an azoxybenzene. In the case of ortho-dimethylated phenylhydroxylamines, such as 2:6-xyllylhydroxylamine and 2:4:6-mesitylhydroxylamine, the stable nitroso-compound is the only product, but 2:5-xyllylhydroxylamine gives a mixture of nitrosoxylenes and azoxyxylenes; in the case of phenylhydroxylamine itself, the condensation proceeds so rapidly that the presence of nitrosobenzene can only be detected by its characteristic odour.

Hydrogen peroxide is always produced in the oxidation, the actual yield being about 90 per cent. of that required for 1 mol.; the  $\beta$ -substituted hydroxylamines are thus among the substances that bring about the increase in activity ('Activirung') of oxygen.

The oxidation proceeds much more rapidly in presence of alkalis, giving rise to the formation of a considerable proportion of nitrobenzene. Similar products are formed in neutral or alkaline solution when the

oxidation is brought about by hydrogen peroxide; this agent has no action on nitrosobenzene in neutral solution, but in alkaline solution readily oxidises it to nitrobenzene; the formation of the latter is therefore probably due to the action of hydrogen peroxide on the nitrosobenzene, which is the first product in both cases.

T. M. L.

**Action of Alkalis on Aromatic Hydroxylamines.** By EUGEN BAMBERGER and FRIEDRICH BRADY (*Ber.*, 1900, 33, 271—274).—Sodium interacts with phenylhydroxylamine in ethereal solution to form the monosodium derivative,  $\text{NHPh}\cdot\text{ONa}$ , a white, crystalline powder; Schmidt's disodium derivative (this vol., i, 20), however, could not be obtained. Cold aqueous sodium hydroxide converts phenylhydroxylamine, when air is excluded almost quantitatively into azoxybenzene and aniline, no trace of nitrobenzene being formed; in dilute solution, the action is very slow, but takes place more rapidly on increasing either the concentration or the amount of alkali, whilst if air is present the action is very rapid, azoxybenzene and nitrobenzene being formed. Since *m*-xylyl-2-hydroxylamine is not acted on by aqueous sodium hydroxide when air is excluded, two methyl groups in the ortho-position relatively to the  $\text{NH}\cdot\text{OH}$  radicle exercise a shielding influence; when air is present, both *m*-xylyl-2-hydroxylamine and mesitylhydroxylamine yield the corresponding nitroso-compounds. It thus appears that, in the case of phenylhydroxylamine, the azoxybenzene is formed by the interaction of the nitrosobenzene initially produced with the base; with *p*-tolylhydroxylamine, indeed, the formation of nitrosotoluene can be detected.

The action of ethyl alcoholic potassium hydroxide in absence of air on phenylhydroxylamine gives, after 10 days, a quantitative yield of azobenzene; with methyl alcohol, the action is similar, but traces of aniline and nitrobenzene are also formed.

W. A. D.

**Aromatic Nitro-derivatives.** By ANGELO ANGELI and FRANCESCO ANGELICO (*Real. Accad. dei Lincei*, 1899, [v], 8, ii, 28—32.)—Whilst substituted hydroxylamines having the substituent in the amino-group react with nitro-compounds with the formation of substances containing the complex  $\cdot\text{NO}\cdot\text{N}\cdot\text{OH}$ , with those in which the substitution is in the hydroxy-group of the hydroxylamine no such reaction takes place. The nature and position of the substituent radicle also influence the nature of the product obtained. Thus, nitrobenzene and *p*-nitrotoluene give rise to the compounds  $\text{Ph}\cdot\text{NO}\cdot\text{N}\cdot\text{OH}$  and  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}\cdot\text{N}\cdot\text{OH}$  respectively. *a*-Nitronaphthalene, however, yields, with hydroxylamine, 1:4-nitronaphthylamine.

When *p*-nitrotoluene reacts with amyl nitrite in presence of sodium ethoxide, the side chain of the toluene is attacked and *p*-nitrobenzaldehyde formed.

T. H. P.

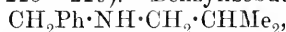
**Action of Sodium and Amyl Alcohol on Phenylaminoacetic Acid.** By ALFRED EINHORN and HERMANN PFEIFFER (*Annalen*, 1899, 310, 218—225. Compare *Abstr.*, 1896, i, 551).—*Phenylisoamylaminoacetic acid*,  $\text{C}_5\text{H}_{11}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , produced on adding sodium to a boiling solution of phenylaminoacetic acid in amyl alcohol, separates from acetic acid as a microcrystalline powder and decom-

poses at  $252^{\circ}$ ; the *nitroso*-derivative crystallises from water in slender white needles and melts at  $109^{\circ}$ .

Benzylisoamylamine,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_5\text{H}_{11}$ , prepared by heating the foregoing acid, is a colourless oil which boils at  $236\text{--}239^{\circ}$  under 720 mm. pressure; the *hydrochloride*, *platinichloride*, and *aurichloride* melt at  $253^{\circ}$ ,  $203^{\circ}$ , and  $190^{\circ}$  respectively. *Catecholcarbonylbenzylisoamylamine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{N}(\text{C}_5\text{H}_{11})\cdot\text{CH}_2\text{Ph}$ , obtained by the action of catechyl carbonate (compare Abstr., 1898, i, 409), crystallises from petroleum in cubes and melts at  $74^{\circ}$ . Benzylisoamylamine is identical with the base described by Zaunschirm (Abstr., 1888, 1077.)

The *acid*,  $\text{C}_8\text{H}_{14}\text{O}_3$ , another product of the action of sodium and amyl alcohol on phenylaminoacetic acid, crystallises in white needles and melts at  $133^{\circ}$ ; the *calcium* salt is microcrystalline. M. O. F.

**Benzylbutylamines.** By ALFRED EINHORN and HERMANN PFEIFFER (*Annalen*, 1899, 310, 225—229).—Benzylisobutylamine,



has been already described by Zaunschirm (Abstr., 1888, 1077); the *hydrochloride* and *aurichloride* melt at  $175^{\circ}$  and  $190^{\circ}$  respectively.

*Benzyl-n-butylamine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\text{Pr}$ , prepared by reducing benzylidenebutylamine in alcoholic solution with sodium amalgam, boils at  $226\text{--}230^{\circ}$  under 715 mm. pressure; the *hydrochloride*, *aurichloride*, and *platinichloride* melt at  $241^{\circ}$ ,  $155^{\circ}$ , and  $90^{\circ}$  respectively.

*Benzyl-sec-butylamine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CHMeEt}$ , obtained from secondary butylamine by the same process, boils at  $218\text{--}225^{\circ}$ ; the *hydrochloride* and *aurichloride* melt at  $180^{\circ}$  and  $185^{\circ}$  respectively.

*Benzyl-tert-butylamine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CMe}_3$ , obtained by the action of trimethylcarbinyl iodide on benzylamine, is a colourless oil; the *hydrochloride*, *platinichloride*, and *aurichloride* melt at  $228^{\circ}$ ,  $221^{\circ}$ , and  $225^{\circ}$  respectively. M. O. F.

**Action of Formaldehyde on o-Nitroaniline.** By JACOB MEYER and MARTIN ROHMER (*Ber.*, 1900, 33, 250—262. Compare Abstr., 1892, 1450, and 1893, i, 389).—*Anhydro-m-nitro-p-aminobenzyl alcohol*,

$(\text{NO}_2\cdot\text{C}_6\text{H}_3\text{<}\begin{smallmatrix}\text{CH}_2\\|\text{NH}\end{smallmatrix})_x$ , is obtained in the form of its hydrochloride either by digesting methylenedi-o-nitraniline with concentrated hydrochloric acid at  $40^{\circ}$  for 1 hour or by warming a mixture of o-nitroaniline, formaldehyde, and hydrochloric acid; the base is produced by digesting its salt with hot water; it is insoluble in all the low boiling point solvents and in dilute acids, dissolves to a slight extent in aniline, quinoline, or pyridine, nitrobenzene, and separates from solution in reddish-brown nodules melting and decomposing at  $265\text{--}270^{\circ}$ . In the above experiment, when the digestion with hydrochloric acid is continued for a longer time at the temperature of the water-bath, the filtrate from the insoluble hydrochloride of the anhydro-compound gradually deposits the hydrochloride of 3:3'-dinitro-4:4'-diaminodiphenylmethane; the base obtained by treating this salt with hot water is extremely insoluble in the ordinary solvents, but dissolves more readily in hot nitrobenzene or phenol, and crystallises in red needles melting at  $228\text{--}230^{\circ}$ ; the substance when pure is quite insoluble in hydro-

chloric acid. Gram (Abstr., 1892, 618), who first studied this compound, gave its melting point as  $224^{\circ}$ , and stated that it dissolved in 20 per cent. hydrochloric acid. The diacetyl derivative melts at  $259-260^{\circ}$ .

*m*-Nitro-*p*-aminobenzyl alcohol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{OH}$ , is obtained as an amorphous yellow precipitate when a solution of the corresponding anhydro-compound in concentrated sulphuric acid is diluted with water; it melts indefinitely, sintering at  $130^{\circ}$  and decomposing at  $180^{\circ}$ ; when dried in a vacuum or when heated with acetic acid, it is reconverted into the anhydride. Tolylenediamine,  $[\text{Me} : (\text{NH}_2)_2 = 1 : 3 : 4]$ , is ultimately obtained by reducing *m*-nitro-*p*-aminobenzyl alcohol with tin and hydrochloric acid, but when less of these reagents

is employed an amorphous base,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \\ \diagup \diagdown \\ \text{CH}_2 \end{smallmatrix}$  (1), is formed as an intermediate product.

3 : 4 : 3' : 4'-Tetraminodiphenylmethane, obtained by reducing 3 : 3'-dinitro-4 : 4'-diaminodiphenylmethane with tin and hydrochloric acid, crystallises from water in colourless, rhombic leaflets which darken on exposure to air and melt at  $137-138^{\circ}$ ; its salts are all extremely soluble, the solution of the hydrochloride developing a dark red coloration with ferric chloride. The authors cannot corroborate Gram's statement that the base is sparingly soluble in water, and that it yields a platinichloride crystallising in yellow needles.

The *di*-2-methylbenziminazole, produced by heating the tetramino-base with glacial acetic acid, contains 1 mol. of water and has the composition  $\text{C}_{17}\text{H}_{18}\text{ON}_4$ ; the water is not removed by treating the substance with concentrated sulphuric acid, acetic anhydride, or phosphorus oxychloride; it melts at  $285^{\circ}$  and when heated at this temperature for some time a portion of the water is driven off. The *platinichloride* crystallises in yellow needles which retain the mol. of water even when dried at  $100^{\circ}$ , the composition of the salt being expressed by  $\text{C}_{17}\text{H}_{18}\text{ON}_4 \cdot \text{H}_2\text{PtCl}_6$ . The *nitrate*,  $\text{C}_{17}\text{H}_{18}\text{O}_6\text{N}_6$ , however, corresponds with the anhydrous iminazole; it decomposes at  $220^{\circ}$ .

The *diiminazole*,  $\text{CH}_2(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix} \text{CH})_2$ , which results from the action of formic acid on the tetramine, crystallises from alcohol in colourless, oval leaflets and melts at  $212^{\circ}$ ; it is very hygroscopic. The *nitrate*,  $\text{C}_{15}\text{H}_{14}\text{O}_6\text{N}_6$ , crystallises in needles melting at  $230^{\circ}$ ; the *platinichloride*,  $\text{C}_{15}\text{H}_{14}\text{ON}_4 \cdot \text{H}_2\text{PtCl}_6$ , contains one molecular proportion of water.

The *di*-2-ethylbenziminazole,  $\text{CH}_2(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix} \text{CEt})_2$ , prepared by heating the tetramine with propionic acid, crystallises from dilute alcohol in colourless prisms and melts at  $263-264^{\circ}$ . The *nitrate* crystallises in colourless needles and melts at  $212^{\circ}$ ; the *platinichloride* separates in sparingly soluble, pale yellow, prismatic crystals.

The *diazimide*,  $\text{CH}_2(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix} \text{N})_2$ , obtained by treating a solution of the tetramine in dilute sulphuric acid with sodium nitrite (2 mols.), crystallises in aggregates of needles and melts at  $155^{\circ}$ ; it

dissolves in sodium hydroxide solution and is reprecipitated by cold dilute acids; it is, however, soluble in hot acids.

The *tetraphenyldiquinoxaline*,  $\text{CH}_2(\text{C}_6\text{H}_3\text{N}(\text{CPh})_2)_2$ , prepared by condensing the tetramine with benzil in alcoholic solution, crystallises from alcoholic chloroform or phenol in clusters of colourless needles and melts at  $245\text{--}247^\circ$ ; it gives the reactions of quinoxaline bases, developing a red coloration on treatment with a mixture of concentrated hydrochloric and sulphuric acids. G. T. M.

**Formation of Quaternary Ammonium Compounds in the case of Homologues of Aniline.** By EMIL FISCHER and ADOLF WINDAUS (*Ber.*, 1900, 33, 345—352).—Von Hofmann observed (this Journal, 1872, 1021) that the dimethyl derivatives of mesidine and pentamethylaminobenzene do not yield quaternary ammonium iodides when heated with methyl iodide at  $150^\circ$ . As a result of examining the six isomeric xylidines, the authors find that 1-amino-2:6-dimethylbenzene is the only member of this class which does not give rise to a quaternary ammonium iodide when the dimethyl base is heated with methyl iodide at  $100^\circ$ ; the immediate neighbourhood of a single methyl group suffices to retard the formation of the quaternary ammonium salt. These phenomena are of the same order as those observed by Victor Meyer in connection with the formation of aromatic esters.

The *methiodide* of dimethyl-*as-m*-xylidine melts and decomposes at  $183^\circ$  ( $186^\circ$  corr.); the *methochloride* is hygroscopic, and forms a *platinichloride* which crystallises in small rhombs. The *methiodide* of dimethyl-*p*-xylidine crystallises from alcohol in small prisms, and decomposes at  $215\text{--}218^\circ$  ( $219\text{--}222^\circ$  corr.); the *platinichloride* dissolves sparingly in water. The *methiodide* of dimethyl-*as-o*-xylidine crystallises from water in long, colourless prisms, and decomposes at  $235\text{--}237^\circ$  ( $240\text{--}242^\circ$  corr.). M. O. F.

**Transformation of Phenyl, *p*-Tolyl, and Thymyl Acetates into the corresponding Benzoates.** By F. BODROUX (*Bull. Soc. Chim.*, 1900, [iii], 23, 54—55).—When phenyl acetate is left in contact with zinc dust and benzoyl chloride at the ordinary temperature, heat is developed, hydrogen chloride evolved, and phenyl benzoate formed in almost the theoretical quantity. *p*-Tolyl and thymyl acetates behave in a similar manner, but the reaction does not occur with  $\beta$ -naphthyl acetate. N. L.

**Synthetical Preparation of Iretol and allied Phentetrol Derivatives.** By EMIL KOHNER (*Monatsh.*, 1899, 20, 926—941).—The author has studied the action of water on derivatives of triaminophenol in order to compare it with the action of water on triaminobenzenes (Weidel, Abstr., 1898, i, 578 *et seq.*).

2:4:6-Triaminophenol, on treatment with water, yields a small quantity of a substance free from nitrogen, which melts at  $164^\circ$ , and may be phentetrol (Oettinger, Abstr., 1895, i, 457). The small yield being probably due to the formation of substances of a quinonoid nature as owing to the presence of a  $\text{NH}_2$  group in the para-position to an OH group, the alkyl derivatives of picric acid were reduced,

2:4:6-Trinitromethoxybenzene, on reduction with tin and hydrochloric acid, at a temperature under  $75^{\circ}$  yields the *dihydrochloride* of diaminohydroxymethoxybenzene, which forms almost colourless needles and gives no coloration with ferric chloride; it forms a *triacetyl* derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OAc})(\text{NHAc})_2$ , which crystallises in colourless needles melting at  $194\text{--}196^{\circ}$ . On treating the dihydrochloride with water containing a little stannous chloride in an atmosphere of carbon dioxide, iretol is obtained. Iretole (de Laire and Tiemann, Abstr., 1894, i, 47) forms a *triacetyl* derivative, which crystallises in needles, melts at  $49^{\circ}$ , and boils at  $230^{\circ}$  under 25 mm. pressure.

2:4:6-Trinitroethoxybenzene, on reduction with tin and hydrochloric acid, yields the *dihydrochloride* of diaminohydroxyethoxybenzene, which crystallises with  $2\text{H}_2\text{O}$ , gives no coloration with ferric chloride or ammonia, and on treatment with water yields 1:2:4:6-*phenetetrol ethyl ether*, which crystallises from water in colourless needles melting at  $220^{\circ}$ . The latter forms a *triacetyl* derivative which melts at  $74^{\circ}$  and boils at  $232^{\circ}$  under 17 mm. pressure. R. H. P.

**Bromination of Phenols.** By HUGO DIRTZ (*Zeit. angew. Chem.*, 1899, 1155—1156).—A reply to Vaubel (this vol., ii, 112). The author discusses the fact that tribromo-*m*-cresol bromide is easily reduced by potassium iodide, although dibromo-*o*- and -*p*-cresol bromides are acted on only with difficulty, but no new facts are adduced. W. A. D.

**A Condensation Product of Trimethylphloroglucinol.** By JAROSLAV CEČELSKY (*Monatsh.*, 1899, 20, 779—791).—*Cedron*,  $\text{C}_{16}\text{H}_{18}\text{O}_6$  or  $\text{C}_{14}\text{H}_{16}\text{O}_5$ , the solid product which separates when aqueous ferric chloride is added to an alcoholic solution of trimethylphloroglucinol (compare Weidel and Wenzel, *Monatsh.*, 1898, 19, 249—267, and Böhm, *Annalen*, 1898, 302, 184), crystallises in aggregates of white, lustreless prisms melting and decomposing at  $305^{\circ}$  (uncorr.), is insoluble in water and ordinary solvents, except at their boiling point, but soluble in dilute alkalis. It is acid to phenolphthalein, and gives a colour reaction with ferric chloride. Although the formula  $\text{C}_{14}\text{H}_{16}\text{O}_5$  is indicated by a cryoscopic determination of the molecular weight,  $\text{C}_{16}\text{H}_{18}\text{O}_6$  is adopted, as it alone agrees with that of the derivatives. The *potassium* compound,  $\text{C}_{16}\text{H}_{18}\text{O}_6\cdot\text{K}_3\cdot 6\text{H}_2\text{O}$ , separates from aqueous solution in well formed, colourless crystals, which rapidly become opaque in the air. *Cedron methylic ether*,  $\text{C}_{16}\text{H}_{17}\text{MeO}_6$ , crystallises from methyl alcohol in white needles melting at  $298^{\circ}$  (uncorr.), is soluble in acetic acid, benzene, or dilute alkalis, but practically insoluble in water.

*Acetylcedron*,  $\text{C}_{16}\text{H}_{17}\text{AcO}_6$ , crystallises from ethyl acetate as small, lustrous prisms, melts at  $260^{\circ}$  (uncorr.), and dissolves with ease only in ethyl acetate and acetic anhydride. *Cedron* does not react with phenylhydrazine, is entirely destroyed by oxidising agents, and if fused with caustic alkali is nearly completely oxidised, only a small quantity of fatty acids (acetic and butyric) being obtained. When heated with hydriodic acid under pressure, an oily compound,  $\text{C}_8\text{H}_{12}\text{O}_3$ , or probably  $\text{C}_{10}\text{H}_{24}\text{O}_6$ , is obtained; this becomes crystalline after a time, boils at  $201\text{--}203^{\circ}$  under 16 mm. pressure, is slightly soluble in water and warm alkali, and has the odour of cedar-wood, whence the

name for the parent substance. When distilled with zinc dust, cedron forms an oil with the odour and boiling point ( $132^{\circ}$ ) of mesityl oxide, but dissimilar in composition; other products of a resinous nature are also obtained.

R. L. J.

**Action of Sodium Mono- and Di-sulphides on Aromatic Nitro-compounds.** By J. J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 271—272).—*o*-Dinitrodiphenyl disulphide,  $S_2(C_6H_4 \cdot NO_2)_2$ , is obtained by the action of sodium disulphide on *o*-dinitrobenzene; similarly, *o*-dinitrodiphenyl sulphide is produced by the action of sodium monosulphide. The aromatic monosulphide oxidises to a sulphoxide, and then to a sulphone, whilst the disulphide yields 2 mols. of *o*-nitrobenzenesulphonic acid. By the action of sodium disulphide on *p*-chloronitrobenzene, *p*-nitrodiphenyl disulphide is produced. The sulphides of sodium reduce *p*-dinitrobenzene to *p*-dinitroazoxybenzene, a small amount of *p*-nitrothiophenol being formed at the same time. Oxidising agents convert *p*-nitrodiphenyl disulphide into *p*-nitrobenzenesulphonic acid.

G. T. M.

**Acidimetry.** By HENRI IMBERT and A. ASTRUC (*Compt. rend.*, 1900, 130, 35—37).—The authors have endeavoured to obtain information as to the relative energy of the acidic functions of various acids, hydroxy-acids, phenols, and their substitution derivatives by means of their reactions with helianthin (*H*), phenolphthalein (*P*), and Poirrier's blue (*B*) respectively. Phenol is neutral to *H* and *P* and monobasic to *B*, whereas trinitrophenol is monobasic with all three. The ordinary monobasic acids are acid to *H* and monobasic with *P* and *B*. It is noteworthy that the heat of neutralisation of trinitrophenol is practically identical with that of the monobasic acids. The bromobenzoic acids are monobasic with *P* and *B*, but only the ortho-derivative is acid to *H*, and the nitrobenzoic acids behave in the same way. Glycollic and lactic acids are monobasic with *P* and *B* and acid to *H*. *o*-Hydroxybenzoic acid is monobasic with all three indicators, but the meta- and para-derivatives, although acid to *H*, cannot be accurately estimated with that indicator, whilst, on the other hand, the para-derivative is dibasic with *B*, and the meta-derivative somewhat more than monobasic. Protocatechuic and vanillic acids are monobasic with *P* and dibasic with *B*. Aminoacetic acid is neutral to *H* and *P*, but acid, although not definitely monobasic, with *B*, the presence of the amino-group reducing the energy of the acidic function. *o*- and *m*-Aminobenzoic acids are likewise almost neutral to *H*, whilst the para-derivative is acid, the amino-group in the para-position having little effect on the energy of the acidic function; all three are monobasic with *P* and *B*.

C. H. B.

**Action of Ethyl Acetoacetate and Substituted Acetoacetates on *p*-Aminobenzoic Acid in Presence and Absence of Pyridine.** By JULIUS TROEGER (*J. pr. Chem.*, 1899, [ii], 60, 507—519).—*Acetoacetyl-p-aminobenzoic acid*,



prepared by heating *p*-aminobenzoic acid with excess of ethyl acetoacetate, crystallises from acetic acid in pale yellow, lustrous needles, melts



at 190°, and is easily soluble in hot water, hot acetic acid, or cold methyl alcohol.

When *p*-aminobenzoic acid and ethyl acetoacetate are heated together in the presence of a little pyridine, a yellowish-white compound,  $C_{18}H_{16}O_5N_2$ , separates, which does not melt, and is almost insoluble in the usual solvents; it probably has the constitution



*Methylacetoacetyl-p-aminobenzoic acid*,  $CHMeAc \cdot CO \cdot NH \cdot C_6H_4 \cdot CO_2H$ , obtained by heating *p*-aminobenzoic acid with ethyl methylacetoacetate, separates from hot water in pale yellow, silky crystals, and melts at 195–196°; the yield is small; if, however, a little pyridine is present, this substance is not formed, but *p*-carbodibenzamic acid is produced. The latter also results from the action of ethyl ethylacetoacetate on *p*-aminobenzoic acid under similar conditions, but in the absence of pyridine no condensation occurs.

When *p*-aminobenzoic acid is heated with excess of ethyl chloroacetoacetate on the water-bath for 1–2 hours only, and the product treated with alcohol, *chloroacetylaceto-p-aminobenzoic acid*,



separates from the alcoholic solution in well-formed crystals; it melts at 189°, and is insoluble in water; if, however, the heating on the water-bath is prolonged, *hydroxyacetoacetyl-p-aminobenzoic acid* is obtained; this is a yellow substance, which melts at 185°, and is soluble in ethyl acetate. The sodium and silver salts were prepared.

E. G.

**Reduction of Benzylaminecarboxylic [Aminophenylacetic] Acids.** By ALFRED EINHORN (*Annalen*, 1899, 310, 189–194. Compare Abstr., 1899, i, 407).—Introductory to the abstracts following, and this vol., i, 221, 222.

M. O. F.

**Reduction of *p*-Benzylaminecarboxylic Acid.** By ALFRED EINHORN and CARL LADISCH (*Annalen*, 1899, 310, 194–204).—

*β*-Hexahydro-*p*-benzylaminecarboxylic acid,  $C_6H_{10} \begin{matrix} \text{CH}_2 \cdot \text{NH}_3 \\ \text{CO-O} \end{matrix}$ , prepared

by reducing *p*-benzylaminecarboxylic acid with sodium and amyl alcohol, crystallises from acetone in small, hygroscopic cubes, and blackens between 220° and 229°, when it evolves gas; when exposed to air during a few minutes, it absorbs moisture, and then melts at 50–78°. It dissolves readily in organic media, but is insoluble in potash, being probably a betaine. The *hydrochloride* and *hydrobromide* are crystalline, and the *hydriodide* contains  $2H_2O$ , which is liberated at 160°. The *platinichloride* crystallises from water in orange plates, and melts, evolving gas, at 234°; the *aureichloride* forms needles, which melt and decompose at 208–223°.

*α*-Hexahydro-*p*-benzylaminecarboxylic acid,  $NH_2 \cdot CH_2 \cdot C_6H_{10} \cdot CO_2H$ , also obtained on reducing *p*-benzylaminecarboxylic acid, is separated from the foregoing substance by taking advantage of the solubility of its hydrochloride in methyl alcohol; it dissolves in alkalis, crystallises from acetone in cubes, and softens at 270°, but does not melt at 280°. The *hydrochloride* crystallises in leaflets and melts at 260°, which is also the melting point of the *platinichloride*; the *aureichloride* crystallises

from hot water, and melts and decomposes at  $150-160^{\circ}$ . The methylic salt yields a *hydrochloride* which separates from ethyl acetate in somewhat indefinite crystals, and melts at  $195-200^{\circ}$ . The *benzoyl* derivative crystallises from alcohol in long needles, and melts at  $177-178^{\circ}$ , when it decomposes.

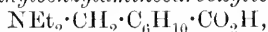
When  $\beta$ -hexahydro-*p*-benzylaminecarboxylic acid is heated with sodium amyloxide in amyl alcohol during 12 hours, it is converted into the  $\alpha$ -modification. Nitrous acid gives rise to the compound,  $C_8H_{14}O_3N_2$ , which crystallises from water in prismatic needles and melts at  $183^{\circ}$ , when it decomposes; it does not give Liebermann's reaction for nitroso-compounds.

The compound,  $C_{16}H_{26}O_4$ , obtained by reducing *p*-methylolbenzoic acid with sodium and amyl alcohol, is insoluble in acetone, chloroform, and benzene; it melts indefinitely at  $140-147^{\circ}$ .

M. O. F.

**Reduction of *p*-Diethylbenzylaminecarboxylic [*p*-Diethylaminophenylacetic] Acid.** By ALFRED EINHORN and STAVROS C. PAPASTAVROS (*Annalen*, 1899, 310, 205—217. Compare Friedländer and Mosezye, *Abstr.*, 1895, i, 414; also Einhorn, *Abstr.*, 1896, i, 551).—*Ethyl  $\omega$ -chloro-*p*-toluate* boils at  $260-280^{\circ}$ . When its alcoholic solution is heated with diethylamine *ethyl p*-diethylbenzylaminecarboxylate,  $NEt_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2Et$ , is produced, forming a colourless oil which boils at  $277-280^{\circ}$ ; the *hydrochloride* crystallises from absolute alcohol in slender, white needles, and melts at  $210^{\circ}$ , the *platinichloride* and *aurichloride* melting at  $213^{\circ}$  and  $134^{\circ}$  respectively. *p*-Diethylbenzylaminecarboxylic acid crystallises from a mixture of alcohol and benzene, and melts at  $150^{\circ}$ ; the *hydrochloride* contains  $2H_2O$ , and melts at  $185^{\circ}$ , whilst the *platinichloride*, *aurichloride*, and *picrate* melt at  $202-203^{\circ}$ ,  $156^{\circ}$ , and  $174-176^{\circ}$  respectively. The *amide* melts at  $152^{\circ}$ , and forms the crystalline *hydrochloride* which melts at  $208^{\circ}$ . Nitro-*p*-diethylbenzylaminecarboxylic acid *hydrochloride*,  $NEt_2 \cdot CH_2 \cdot C_6H_3(NO_2) \cdot CO_2H \cdot HCl$ , prepared by the action of diethylamine on the nitro-derivative of  $\omega$ -chloro-*p*-toluic acid, crystallises from alcohol in small prisms and melts at  $225^{\circ}$ .

*trans*-Hexahydro *p*-diethylbenzylaminecarboxylic acid,



obtained by reducing *p*-diethylbenzylaminecarboxylic acid with sodium in amyl alcohol, melts indefinitely at  $85-90^{\circ}$ ; the *hydrochloride* and *aurichloride* melt at  $195^{\circ}$  and  $153^{\circ}$  respectively, and the *picrate* melts at  $163-164^{\circ}$ .

*cis*-Hexahydro-*p*-diethylbenzylaminecarboxylic acid, another product of the reduction of *p*-diethylbenzylaminecarboxylic acid, has probably the betaine-like constitution,  $C_6H_{10} \begin{matrix} < CH_2 \cdot NHEt_2 \\ & CO-O \end{matrix}$ ; it is obtained from the *trans*-modification by the action of sodium amyloxide in hot amyl alcohol; it is a colourless oil with a stupefying odour, and boils at  $275-280^{\circ}$ ; the *hydrochloride* and *picrate* melt at  $166^{\circ}$  and  $163^{\circ}$  respectively, and the *aurichloride* crystallises in golden-yellow, prismatic needles. The *ethyl* ester is an oil, and the *methylammonium hydroxide*,  $C_{11}H_{21}O_3N$ , crystallises from alcohol and ethyl acetate in

needles melting at  $142^{\circ}$ ; when the latter is heated with concentrated potassium hydroxide, the unsaturated acid,  $C_8H_{10}O_2$ , is produced, crystallising from petroleum in needles which melt at  $164^{\circ}$ . M. O. F.

**Phenylisobutyric and Tolylisobutyric Acids.** By OTTO WALLACH (*Chem. Centr.*, 1899, ii, 1047—1048; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—*α-Phenylisobutyric acid*,  $CM_2Ph \cdot CO_2H$ , prepared by the action of aluminium bromide on *α*-bromoisobutyric acid and benzene, melts at  $77-78^{\circ}$ , boils at  $150-155^{\circ}$  under 10 mm. pressure, and forms an insoluble silver salt and a calcium salt which crystallises with  $2H_2O$ . The *methyl* ester boils at  $225^{\circ}$ , the *ethyl* ester at  $235-236^{\circ}$ , the *propyl* ester at  $250^{\circ}$ , and the *butyl* ester at  $260-261^{\circ}$ . The *chloride* boils at  $109^{\circ}$  under 13 mm. pressure; the *amide* melts at  $160-161^{\circ}$ , boils at  $200-205^{\circ}$  under 80 mm. pressure, and is almost insoluble in water and only very slightly soluble in ether. *Phenylisobutyronitrile*,  $CM_2Ph \cdot CN$ , obtained by the action of phosphorus pentachloride on the amide, boils at  $232^{\circ}$ ; has a sp. gr. 0.966 at  $21^{\circ}$ , and a specific refractive index  $n_D$  1.50665. By the action of phosphoric oxide on the amide, a hydrocarbon is formed which is probably *diphenyltetramethylethane*,  $CM_2Ph \cdot CMe_2Ph$ ; it melts at  $55-56^{\circ}$ , and boils at  $138-140^{\circ}$  under 15 mm. pressure. *Phenylisobutylamine*,  $CM_2Ph \cdot CH_2 \cdot NH_2$ , prepared by reducing the nitrile, is a colourless oil, and forms a hydrochloride which is very easily soluble in water. The *carbamide*,  $CM_2Ph \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$ , obtained by the action of potassium cyanate on the hydrochloride, crystallises in transparent plates and melts at  $140-141^{\circ}$ .

*p-Tolylisobutyric acid*,  $C_6H_4Me \cdot CM_2 \cdot CO_2H$ , prepared in a similar manner to phenylisobutyric acid, melts at  $72^{\circ}$ , and boils at  $172-180^{\circ}$  under 12 mm. pressure. The *amide* melts at  $123-124^{\circ}$ , and boils at  $240-247^{\circ}$  under 84 mm. pressure. *p-Tolylisobutyronitrile* boils at  $247-248^{\circ}$ , has a sp. gr. 0.955 at  $20^{\circ}$ , a specific refractive index  $n_D$  1.5057, and by the action of phosphoric oxide yields *p*-isobutyltoluene. E. W. W.

**Chlorylphthalimide and Bromylphthalimide and their Conversion into Isatoic Anhydride and Acetylanthranil.** By JULIUS BREDT and H. HOF (*Ber.*, 1900, 33, 21—29).—*Bromylphthalimide*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} NBr$ , is obtained by running a solution of phthalimide in a slight excess of dilute aqueous sodium hydroxide into a mixture of bromine and water; *chlorylphthalimide*, by adding the first solution gradually to water through which chlorine, kept constantly in excess, is being passed; all solutions are kept at  $0^{\circ}$ . The two substances melt at  $206-207^{\circ}$  and  $183-185^{\circ}$  respectively; they lose their halogen readily, forming hypochlorous or hypobromous acid, or derivatives of these. When allowed to remain in dilute alcoholic solution with sodium methoxide or ethoxide, at first at  $0^{\circ}$ , they yield *dimethyl* and *diethyl carboxyanthranilates* (isatoates), which melt at  $60-61^{\circ}$  and  $43-44^{\circ}$  respectively, and boil, the first at  $165-166^{\circ}$  under 12 mm., the second at  $174^{\circ}$  under 10 mm. pressure. When a concentrated sodium methoxide solution is employed, a carbamide derivative,  $CO(NH \cdot CO \cdot C_6H_4 \cdot CO_2Me)_2$ , is the chief product; it melts

and decomposes at 142—143°, and crystallises with chloroform. The diethyl ester, when allowed to remain with a suitable quantity of sodium ethoxide in alcoholic solution, yields ethyl hydrogen carboxyanthranilate,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , which melts and decomposes at 126°. When this is boiled with acetic anhydride, it yields *acetyl-anthranil*,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{N}^{\text{Ac}} \\ \text{CO}\end{smallmatrix}\right\rangle$ , which melts at 79—80°, boils at 148—149° under 13 mm. pressure, and yields acetylanthranilic acid when boiled with water. If acetyl chloride is employed instead of acetic anhydride, the product is isatoic anhydride,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CO} \\ \text{CO}\end{smallmatrix}\right\rangle\text{O}$ , in good yield (compare Erdmann, *Abstr.*, 1899, i, 939). This forms monoclinic plates [ $a:b:c=0.7029:1:0.6797$ ;  $\beta=86^\circ 25'$ ]; when it is heated with alcoholic sodium alkoxides, alkyl anthranilates are formed and other products in addition; the *isobutyl* and *amyl* esters boil respectively at 156—157° and 169—170° under 13½ mm. pressure. C. F. B.

**Formation of Indigo from Woad (*Isatis tinctoria*).** By MARTINUS W. BEIJERINCK (*Proc. k. Akad. Wetensch. Amsterdam*, 1899, 2, 120—129).—*Indigofera leptostachya* and *Polygonum tinctorium* contain indican; woad, on the other hand, contains free indoxyl. The extraction of woad must be carried out in the absence of air owing to the unstable nature of the indoxyl; hot and cold extracts of the plant both contain this compound. The indoxyl solution obtained either from the indican plants by the action of an enzyme or from woad, is fluorescent and slightly acid; a film of indigotin is slowly produced on its surface, the oxidation being accelerated by alkalis, and to a less extent by acids. Hydrogen peroxide destroys indoxyl, but without forming coloured products. A precipitate of indigo-red is produced by warming an acid or alkaline solution of indoxyl with isatin; a similar result is obtained with an acid solution of indican, and the reaction may be employed in estimating the glucoside. The indigo from woad contains a small quantity of indigo-red. The indigo plants do not appear to contain an oxydase capable of converting indoxyl into indigotin, and this pigment is not produced in their tissues when they are suddenly killed. A large amount of colouring matter, however, is formed when the plants are allowed to die slowly, and the author supposes the oxidation to be due to the formation of alkali in the dying tissues.

When the “indican plants” are asphyxiated at the ordinary temperature by immersion in mercury or exposure to hydrogen or carbon dioxide, the indigo enzyme converts the indican into indoxyl; these dead plants then resemble woad under normal conditions, and, like the latter, yield a large amount of indigo on exposure to an atmosphere containing ammonia. G. T. M.

**Formation of Indigo from Indigoferæ and from *Marsdenia tinctoria*.** By PIETER VAN ROMBURGH (*Proc. k. Akad. Wetensch. Amsterdam*, 1899, 2, 344—348).—The aqueous extract of the leaves of *Marsdenia tinctoria* and certain of the *Indigoferæ* contains a soluble substance yielding indigotin on oxidation; indigo leaves retain the

power of decomposing indican even after extraction with ether, alcohol, acetone, or chloroform; the soluble compound which is thus liberated differs from indigo-white in being soluble in acids, and from indoxyl in its reactions with mineral acids or alkaline carbonates. G. T. M.

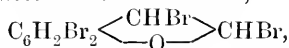
**Fusion of Indigotin with Potassium Hydroxide.** By W. HENTSCHEL (*J. pr. Chem.*, [ii], 1899, 60, 577—581. Compare Heumann and Bachofen, *Abstr.*, 1893, i, 270; Fritsche and Liebig, *Annalen*, 1841, 39, 76; Cahours, *Ann. Chim. Phys.*, 1845, [iii], 13, 113).—Indigo-blue dissolves but slowly in hot concentrated potassium hydroxide; at 150°, the products are indoxyl and chrysanic acid,  $C_{16}H_{12}O_4N_2$ , obtained respectively by reduction and oxidation of the indigotin. At 200—300°, the chrysanic acid becomes converted into anthranilic acid, but the indoxyl remains unaltered even at temperatures at which the anthranilic acid itself begins to decompose. The only bye-products are hydrogen and carbon dioxide. The action with sodium hydroxide is more violent; at 200°, the chief product is chrysanic acid, together with a little indoxyl; at 250°, practically pure anthranilic acid is obtained. J. J. S.

**Salts of Indigotintrisulphonic Acid.** By MAX HÖNIG (*Chem. Centr.*, 1899, ii, 1052; from *Festschr. Techn. Hochschule Brünn*, October, 1899).—The salts of indigotin-monosulphonic and -disulphonic acids are slightly soluble in water and are difficult to obtain in a crystalline form. Majumdar prepared sodium indigotindisulphonate in the form of small needles arranged in tufts, but all the other salts were amorphous. *Indigotintrisulphonic acid* is formed by heating indigo with fuming sulphuric acid at 40—50°. The alkali salts are prepared by neutralising the aqueous solution of the acid, salting out with the corresponding alkali chloride, and crystallising from hot dilute alcohol. The sodium salt,  $C_{16}H_7O_2N_2(SO_3Na)_3$ , crystallises in copper-red, monoclinic needles which have a metallic lustre; it is easily soluble in hot 65 per cent. alcohol or in cold water, forming a solution which appears bluish-violet in reflected, and purple-red in transmitted, light. The potassium salt forms glittering, dark bluish-violet, rhombic leaflets and is rather soluble in water. The ammonium salt forms dark blue masses of very small crystals, and is very readily soluble in water or alcohol. The barium salt separates as a pale blue, crystalline precipitate somewhat soluble in water, but insoluble in barium chloride solution. The lead salt is a pale blue, amorphous precipitate and is rather soluble in water. The sodium or potassium salt can be titrated with centinormal potassium permanganate solution and might therefore be of use in the Neubauer-Löwenthal method of determining tannin, or in the Marx-Trommsdorff method of estimating nitric acid. E. W. W.

**Tribromocoumarin and its Derivatives.** By HUGO SIMONIS and G. WENZEL (*Ber.*, 1900, 33, 421—425).—Coumarin, when heated at 170° in a sealed tube with bromine, water, and some iodine, yields *tribromocoumarin*,  $C_9H_2Br_3$   $\begin{matrix} \text{CH:CHBr} \\ | \\ \text{O}-\text{CO} \end{matrix}$ , which forms long needles melting at 196°; on hydrolysing this with alcoholic potash,  *dibromo-*

*coumarilic acid*,  $C_6H_2Br_2\langle\begin{smallmatrix} CH \\ -O- \end{smallmatrix}\rangle C\cdot CO_2H$ , is obtained which crystallises in long needles melting at  $276^\circ$ ; the *potassium* and *sodium* salts crystallise with  $2H_2O$ , the *barium* and *copper* salts with  $4H_2O$ ; the *methyl* ester separates from methyl alcohol in white needles melting at  $151^\circ$ , and boils above  $360^\circ$  without decomposition.

*Dibromocoumarone*, obtained by heating dibromocoumarilic acid, crystallises in colourless needles melting at  $57.5^\circ$ , and on treatment with bromine yields *dibromocoumarone dibromide*,



which forms colourless, prismatic crystals melting at  $108^\circ$ . Tribromocoumarin, on treatment with ammonia, yields the *amide* of dibromo- $\alpha$ -aminocoumaric acid,  $OH\cdot C_6H_2Br_2\cdot CH:C(NH_2)\cdot CO\cdot NH_2$ , which forms prismatic crystals melting at  $184^\circ$ , and on hydrolysis yields an acid easily soluble in water.

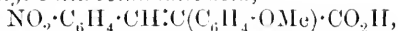
R. H. P.

**Constitution of Naphthoylbenzoic Acid, Naphthanthraquinone, and Naphthanthracene.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, **33**, 446—469. Compare Abstr., 1898, i, 481 and 482).—*a*-Naphthoyl-*o*-benzoic acid is conveniently prepared by adding aluminium chloride to a hot solution of phthalic anhydride and naphthalene in carbon disulphide; its constitution is indicated from the results of fusion with potash, *a*-naphthoic acid being one of the products of hydrolysis. Naphthanthraquinone is shown to be an  $\alpha\beta$  compound by fusing it with potash,  $\beta$ -naphthoic and benzoic acids being thereby produced; it follows that naphthanthracene must also be an  $\alpha\beta$ -derivative.

G. T. M.

**Syntheses in the Phenanthrene Series: Synthesis of 1- and 3-Methoxyphenanthrene.** By ROBERT PSCHORR, O. WOLFES, and W. BUCKOW (*Ber.*, 1900, **33**, 162—176).—Saligenin methyl ether (*o*-methoxybenzyl alcohol) is best prepared by leaving saligenin in contact with methyl iodide, methyl alcohol, and potassium hydroxide for 3 days at the ordinary temperature (compare Cannizzaro and Körner, *Ber.*, 1872, **5**, 436); at a higher temperature, *o*-methoxybenzyl methyl ether,  $OMe\cdot C_6H_4\cdot CH_2\cdot OMe$ , boiling at  $229$ — $230^\circ$ , is obtained. *o*-Methoxybenzyl chloride forms six-sided plates, melts at  $29$ — $30^\circ$ , and boils at  $110$ — $112^\circ$  under 11 mm. pressure; it decomposes with loss of hydrogen chloride on keeping, forming a rose-coloured, brittle, vitreous mass. *o*-Methoxyphenylacetoneitrile, prepared by heating the chloride with dilute alcoholic potassium cyanide, crystallises from benzene on adding light petroleum in long, thin prisms, melts at  $68^\circ$ , boils at  $141$ — $143^\circ$  under 15 mm. pressure, and has a peculiar, suffocating odour. There is also formed simultaneously a considerable quantity of *o*-methoxybenzylethyl ether, which, however, is best prepared by heating *o*-methoxybenzyl chloride with alcoholic sodium ethoxide; it is a colourless, strongly-refracting liquid, which boils at  $230$ — $232^\circ$  under 754 mm. pressure. *o*-Methoxyphenylacetic acid,  $OMe\cdot C_6H_4\cdot CH_2\cdot CO_2H$ , obtained by hydrolysing the nitrile, crystallises from water in colourless, flattened prisms and melts at  $124^\circ$ .

*o*-*o*-Methoxyphenyl-*o*-nitrocinnamic acid,



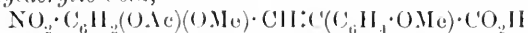
prepared by Perkin's reaction from *o*-methoxyphenylacetic acid and *o*-nitrobenzaldehyde, crystallises from alcohol in yellowish plates, melts at 219—220° (corr.), and on reduction with ferrous hydroxide yields the corresponding *amino*-acid; this crystallises from alcohol in yellowish prisms and melts at 169° (corr.). On decomposing its diazo-sulphate with copper powder, water and nitrogen are eliminated (compare Pschorr, Abstr., 1896, i, 303), and 1-methoxyphenanthrene-10-carboxylic acid obtained; the latter crystallises from alcohol in lustrous, slightly yellow leaflets, melts at 215° (corr.), and yields crystalline *barium*, *silver*, *lead*, *copper*, *platinum*, and *iron* salts. When distilled under 150—200 mm. pressure, carbon dioxide is evolved and 1-methoxyphenanthrene formed; this crystallises from alcohol in long, silky needles, sinters at 103°, and melts at 105—106°; the *picrate*,  $\text{C}_{21}\text{H}_{15}\text{O}_8\text{N}_3$ , crystallises from alcohol in tufts of yellowish-red needles and melts at 153° (corr.). Attempts to oxidise 1-methoxyphenanthrene and its carboxylic acid to the corresponding phenanthraquinones gave rise only to yellow, intractable, amorphous products.

*Methyl p*-methoxyphenylacetate,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , prepared by heating *p*-hydroxyphenylacetic acid with methyl iodide (2 mols.), potassium hydroxide, and methyl alcohol, boils at 263—265° under 760 mm., and at 155—157° under 23 mm. pressure.

*o*-*p*-Methoxyphenyl-*o*-nitrocinnamic acid crystallises from toluene in short golden prisms, from alcohol in lustrous plates, and melts at 177° (corr.); on reduction, it yields the *amino*-acid,  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{N}$ , which crystallises from alcohol in long, yellow prisms mixed with colourless granules. Both modifications melt at the same temperature and have the same composition, moreover the colourless granules on heating are apparently converted into the yellow variety, and it is worthy of note that *o*-phenyl-*o*-aminocinnamic acid exists in two similar modifications (Pschorr, *loc. cit.*). 3-Methoxyphenanthrene-10-carboxylic acid, prepared in the same way as 1-methoxyphenanthrene-10-carboxylic acid, crystallises from alcohol in nearly colourless, lustrous needles, melts at 239°, and on being fused for a short time, and subsequently distilled in a vacuum, is partially decomposed into 3-methoxyphenanthrene. This crystallises from dilute alcohol in lustrous plates, melts at 63° and yields a *picrate*, which forms red needles melting at 124.5° (corr.). 3-Methoxyphenanthraquinone, prepared by oxidising 3-methoxyphenanthrenecarboxylic acid with chromic acid in acetic acid solution, crystallises from alcohol in orange needles and melts at 208° (corr.).

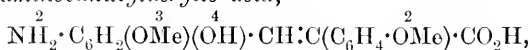
W. A. D.

Syntheses in the Phenanthrene Series;  $\psi$ -Thebaol. By ROBERT PSCHORR (*Ber.*, 1900, 33, 176—183).—*o*-*o*-Methoxyphenyl- $\beta$ -*o*-nitroacetylvanillylacrylic acid,



$[\text{CH} : \text{NO}_2 : \text{OMe} : \text{OAc} = 1 : 2 : 3 : 4]$ , prepared by Perkin's reaction from *o*-methoxyphenylacetic acid (preceding abstract) and nitroacetylvanillin  $[\text{CHO} : \text{NO}_2 : \text{OMe} : \text{OAc} = 1 : 2 : 3 : 4]$ , crystallises from toluene in feebly yellow prisms, sinters at 210°, melts at 217—218° (corr.), and

on reduction with ammoniacal ferrous hydroxide yields *α*-*o*-methoxyphenyl-β-*o*-aminovanillylacrylic acid,

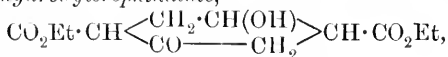


which sinters at 60°, melts at about 90°, and cannot be recrystallised as it is easily decomposed; in toluene solution, the composition gives rise to 2 : 7-*dihydroxy-8-methoxy-3-*o*-methoxyphenylquinoline*, which separates in nearly colourless prisms and melts at 255—256° (corr.). *α*-*ψ*-Thebaolcarboxylic acid (6-hydroxy-1 : 5-dimethoxyphenanthrene-10-carboxylic acid), prepared from the foregoing amino-acid by the method adopted for 1-methoxyphenanthrene-10-carboxylic acid (preceding abstract), crystallises from dilute alcohol or acetic acid in nearly colourless, six-sided plates, and melts at 231° (corr.); the *acetyl* derivative,  $\text{OAc}\cdot\text{C}_{14}\text{H}_6(\text{OMe})_2\cdot\text{CO}_2\text{H}$ , prepared by acting on the potassium salt of the acid with acetic anhydride, crystallises from the same solvents in flat prisms and melts at 220—227° (corr.); if, however, the hydroxy-acid is warmed with acetic anhydride containing a small quantity of concentrated sulphuric acid, the *anhydride*,  $\text{C}_{38}\text{H}_{30}\text{O}_{11}$ , of the acetyl derivative is obtained, which crystallises from glacial acetic acid in irregular leaflets and melts at 236—238°.

*α*-*ψ*-Thebaol (6-hydroxy-1 : 5-dimethoxyphenanthrene), prepared by heating its carboxylic acid with acetic acid for 5 hours at 215—225°, crystallises from dilute alcohol or glacial acetic acid in reddish-brown, irregular leaflets, melts at 164—165° (corr.), and yields a *sodium* salt crystallising in lustrous leaflets; the *acetyl* derivative,  $\text{C}_{18}\text{H}_{16}\text{O}_4$ , forms colourless, radiating prisms, melts at 96—97°, and, when heated with acetic anhydride containing a little concentrated sulphuric acid, yields a blackish-blue, crystalline powder, which contains sulphur and resembles indigo in appearance. 1 : 5 : 6-*Trimethoxyphenanthrene*, prepared by heating *ψ*-thebaol with methyl iodide and potassium hydroxide, crystallises from alcohol in colourless leaflets and melts at 135° (corr.); the *picrate*,  $\text{C}_{23}\text{H}_{19}\text{O}_{10}\text{N}_3$ , forms dark-red, lustrous needles and melts at 126° (corr.), whilst the *dibromo*-derivative,  $\text{C}_{14}\text{H}_5\text{Br}_2(\text{OMe})_3$ , crystallises from glacial acetic acid in nearly colourless needles melting at 139—141° (corr.).

Since both 1 : 5-dimethoxy-6-acetoxypheanthrene and its 10-carboxylic acid resemble 1-methoxyphenanthrene (preceding abstract) in not yielding the corresponding phenanthraquinones on oxidation, and differ in this respect from 3-methoxyphenanthrenecarboxylic acid (preceding abstract) and acetylthebaol (Freund, Abstr., 1897, i, 495), it appears probable that thebaol does not contain a methoxyl group in position 1, but is either 4 : 5- or 4 : 7-dimethoxy-6-hydroxyphenanthrene (compare Freund, *loc. cit.*). W. A. D.

**Hydrogenisation of Ethyl Succinylsuccinate.** By ROBERT STOLLÉ (*Ber.*, 1900, 33, 390—392).—*Ethyl dihydrosuccinylsuccinate* or *tetrahydrodihydroxyterephthalate*,



or  $\text{CO}_2\text{Et}\cdot\text{C}\begin{matrix} \text{CH}_2\cdot\text{CH}(\text{OH}) \\ \text{C}(\text{OH}) \quad \text{CH}_2 \end{matrix}\text{CH}\cdot\text{CO}_2\text{Et}$ , a viscous oil which boils



at 218—220° under 14 mm. pressure, dissolves sparingly in water, and reduces alkaline permanganate; the alcoholic solution is indifferent towards ferric chloride. The *methyl* ester boils at 211—212° under 14 mm. pressure.

*Ethyl tetrahydrosuccinylsuccinate* (*hexahydrodihydroxyterephthalate*,  $\text{CO}_2\text{Et} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol, and melts at 135—136°; it is somewhat soluble in water, and is indifferent towards alkaline permanganate. The *methyl* ester melts at 187°.

*Ethyl hydrogen dihydroterephthalate*,  $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \\ \text{CH} \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , crystallises from alcohol in slender needles, and melts at 178—179°.  
M. O. F.

**Usnic Acid.** By OSKAR WIDMAN (*Annalen*, 1899, 310, 230—264).—Usnic acid has been isolated from a large number of lichens, and the descriptions of various specimens differ somewhat widely among themselves. This is explained by the fact, discovered by the author, that usnic acid occurs in two modifications, which are optical antipodes; these melt at 203°, and the inactive mixture melts at 192°. So far as can be ascertained from existing data, the character of the usnic acid produced by a lichen is not influenced by position, latitude, height above sea-level, or season of year.

*d*-Usnic acid,  $\text{C}_{18}\text{H}_{16}\text{O}_7$ , found in several varieties of *Usnea barbata*, melts at 203°; specimens prepared from *U. barbata hirta*, *U. barbata γ-plicata*, and *Cladonia rangiferina silvatica*, gave  $[\alpha]_D + 49.2^\circ$ ,  $49.3^\circ$ , and  $49.55^\circ$  respectively. *l*-Usnic acid also melts at 203°, and gave  $[\alpha]_D - 49.58^\circ$  and  $-48.55^\circ$ , according as the source was *Cetraria nivalis* or *Cladonia rangiferina alpestris*. *i*-Usnic acid crystallises from benzene and acetic acid in yellow needles, long, four-sided prisms, or six-sided plates, and melts at 191—192°. The *sodium* salts contain  $2\text{H}_2\text{O}$ , which is easily removed in the case of the active compound.

The *d*- and *l*-oximes of usnic acid melt and slowly decompose at 100—145°. The *anhydride*,  $\text{C}_{18}\text{H}_{15}\text{O}_6\text{N}$ , prepared by heating *d*-usnic acid in benzene with hydroxylamine acetate, crystallises from ethyl acetate in long, lustrous prisms or four-sided plates, and melts at 230° without evolving gas; sodium methoxide converts it into the *compound*,  $\text{C}_{19}\text{H}_{19}\text{O}_7\text{N}$ , which crystallises in quadratic prisms and melts at 147°. The *inactive oxime* crystallises in prismatic needles, and melts and decomposes at 243—244°; the *acetyl* derivative forms pale yellow leaflets and melts at 194°, when it evolves gas.

The *d*- and *l*-semicarbazones of usnic acid decompose suddenly at 219—220°, and the *inactive* modification decomposes at 211°.

The *d*-*anilide* separates from a mixture of benzene and petroleum in four-sided pyramids, and usually melts at 138°, but the melting point is sometimes as high as 152—153°, or even 157—158°, if the substance is previously dried at 110°. It has  $[\alpha]_D + 28.6^\circ$  in chloroform, and the *l*-*anilide*, which resembles it, has  $[\alpha]_D - 28.45^\circ$ . The *inactive anilide* crystallises from glacial acetic acid in cubes, and melts at

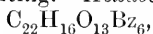
232°. The *d-oximeanilide*,  $C_{24}H_{22}O_5N_2$ , prepared from the *d-anilide* by the action of hydroxylamine, dissolves in potassium hydroxide, and melts at 222—230°.

The *inactive amide*,  $C_{18}H_{17}O_6N$ , obtained by heating *i-usnic acid* with alcoholic ammonia in a reflux apparatus, crystallises from glacial acetic acid in rhombic plates, and melts at 245—246°. The *piperidine* salt of *i-usnic acid* crystallises in leaflets, and gradually dissolves at 140°.

The *bisphenylhydrazide anhydride* of *d-usnic acid*,  $C_{30}H_{26}O_4N_4$ , crystallises from glacial acetic acid and melts at 233°, and is identical with the phenylhydrazine derivative of "*α-usnic acid*" described by Hesse. The *bisphenylhydrazide anhydride* of *i-usnic acid* melts at 267°. The *m-p-toluylenediamide* of *i-usnic acid* separates from glacial acetic acid in somewhat indefinite crystals, and melts at 217°, when it blackens and evolves gas.

M. O. F.

**Derivatives of Carminic Acid.** By CARL LIEBERMANN, P. HÖRING, and FRITZ WIEDERMANN [and in part MESSINGER and I. FRÄNCKEL] (*Ber.*, 1900, 33, 149—159. Compare Abstr., 1898, i, 682).—Carminic acid forms an *acid silver* salt,  $C_{22}H_{21}O_{13}Ag$ , obtained as an orange-coloured precipitate on the addition of silver nitrate to an alcoholic solution of the acid. The *ethylamine* salt,  $C_{22}H_{22}O_{13}(NH_2Et)_3$ , and the *benzylamine* salt,  $C_{22}H_{22}O_{13}(NH_2 \cdot C_6H_5)_3$ , both form small, brown needles and dissociate on heating. *Hexabenzoylcarminic acid*,



is obtained by the action of benzoyl chloride on carminic acid, and forms an orange-red powder which is only slowly dissolved by alkalis.

The first product of the action of bromine on carminic acid dissolved in acetic acid is *dibromocarminic acid hydrobromide*,  $C_{22}H_{20}O_{13}Br_2 \cdot HBr$ ; it forms small, lemon-yellow crystals which easily evolve hydrogen bromide and carbon dioxide, and give *decarboxydibromocarminic acid*,  $C_{21}H_{20}O_{11}Br_2$ . This is obtained in the form of small, hygroscopic needles and has colouring properties similar to those of cochineal; its formation affords a proof of the presence of a carboxyl group in carminic acid, which, however, cannot owe its colouring properties to this group. The *hexa-acetyl* derivative is an orange-red powder, and the *hexabenzoyl* derivative is precipitated from benzene by light petroleum as an orange-red powder which melts at 160—170° and is insoluble in alkalis.

The authors have repeated the experiments of Will and Leymann (Abstr., 1886, 252) on *α*- and *β*-bromocarmin. *β*-Bromocarmin forms well-characterised salts with aromatic bases; the *p-toluidine* salt is precipitated in the form of red needles on mixing a solution of *β*-bromocarmin with the base, and serves to separate it from *α*-bromocarmin, which only forms a similar salt with difficulty. R. H. P.

**Allotropy of Benzophenone.** By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, 130, 40—42).—When benzophenone is dissolved in dilute alcohol and a current of air passed through the solution for many weeks, the liquid being protected from light, the benzophenone is converted into the unstable modification melting at

27°. No similar change is produced by exposing the crystallised substance to light. Rapid dissolution of the benzophenone in dilute alcohol facilitates the conversion into the allotropic modification. It is noteworthy that in these experiments the benzophenone is not oxidised.

C. H. B.

**Dibenzylideneacetoneoxime.** By GAETANO MINUNNI (*Gazzetta*, 1899, 29, ii, 387—404. Compare Abstr., 1898, i, 194).—The compound, melting at 142—144°, obtained by the action of hydroxylamine hydrochloride on dibenzylideneacetone, and described (*loc. cit.*) as a dihydroisoxazole derivative, proves to be *dibenzylideneacetoneoxime*,  $C(CH:CHPh)_2 \cdot N \cdot OH$ ; it forms an *acetyl* and a *benzoyl* derivative, which crystallise from alcohol in beautiful, silky, white needles, the former melting at 93—94° and the latter at 111·5—112°.

*Dibenzylideneacetonephenylhydrazone*,  $C_{23}H_{20}N_2$ , obtained by the action of phenylhydrazine on either the acetone or its oxime, separates from alcohol in tufts of yellow needles melting at 146·5—147·5°.

The action of concentrated sulphuric acid on dibenzylideneacetoneoxime gives rise to an isomeric substance which crystallises from alcohol in beautiful, white, nacreous leaflets melting at 110—111°; it is insoluble in alkalis or dilute mineral acids.

In the dibenzylideneacetoneoxime mother liquors, two other compounds are found: one,  $C_{17}H_{18}O_2N_2$ , melting at 200—202° (*loc. cit.*), and the other having the same composition and separating from its ethereal solution by the addition of light petroleum in the form of star-shaped crystals melting at 163—164°.

T. H. P.

**Action of Hydroxylamine Hydrochloride on Ketones of the Type  $CO(CH:CHR)_2$  in presence of Sodium Acetate.** By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 404—420).—The compound,  $C_{17}H_{18}O_2N_2$ , melting at 200—202°, obtained from the dibenzylideneacetoneoxime mother liquors (see preceding abstract), is shown to be *α-dibenzylideneacetonehydroxylamineoxime*, having the constitution  $OH \cdot NH \cdot CHPh \cdot CH_2 \cdot C(N \cdot OH) \cdot CH:CHPh$  or  $CH_2Ph \cdot CH(NH \cdot OH) \cdot C(N \cdot OH) \cdot CH:CHPh$ ; the *dibenzoyl* derivative,  $C_{31}H_{26}O_4N_2$ , separates from alcohol in acicular crystals melting at 147—148°, which become slightly red on exposure to the air. The *diacetyl* compound,  $C_{21}H_{22}O_4N_2$ , crystallises from alcohol in white, acicular needles melting at 156—157°. By the action of hydrochloric acid on the *α*-oxime, hydroxylamine, dibenzylideneacetone, and benzaldehyde are formed, together with the *β* modification melting at 164°, which is also found in the benzylideneacetoneoxime mother liquors (*loc. cit.*).

Dipiperonalacetone reacts with hydroxylamine hydrochloride in presence of sodium acetate in a manner similar to dibenzylideneacetone, a compound,  $C_{19}H_{18}O_6N_2$ , being obtained; it separates from alcohol in pale yellow, mammillary masses melting at 177—179°.

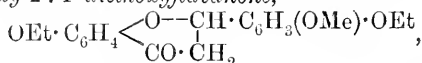
T. H. P.

**3:3'-Dihydroxyflavone.** By B. VON HARPE and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 322—325).—*2'-Hydroxy-3:4'-diethoxychalkone*,  $OEt \cdot C_6H_3(OH) \cdot CO \cdot CH:CH \cdot C_6H_4 \cdot OEt$ , obtained by the condensation of *m*-ethoxybenzaldehyde and 2 hydroxy-4-ethoxyacetophenone

under the conditions described previously (Abstr., 1898, i, 369), crystallises from alcohol in yellow plates melting at  $85^{\circ}$ , dissolves in concentrated sulphuric acid to a deep yellow solution, yields a sparingly soluble *sodium* salt, and an *acetyl* derivative melting at  $68^{\circ}$ . The *acetyl dibromide*,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OAc}) \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ , crystallises from alcohol in colourless needles melting at  $105^{\circ}$ , and, when warmed in alcoholic solution with concentrated potassium hydroxide, is converted into 3 : 3'-*diethoxyflavone*,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ | \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ . This crystal-

lises from dilute alcohol in colourless needles melting at  $153-154^{\circ}$  and is soluble in concentrated sulphuric acid to a pale yellow solution with a bluish-green fluorescence; when hydrolysed with sodium ethoxide, it is quantitatively converted into *m*-ethoxybenzoic acid and 2-hydroxy-4-ethoxyacetophenone, and when boiled for two hours with hydriodic acid of sp. gr. 1.96, it yields 3'-*hydroxy-3-ethoxyflavone*, which crystallises in colourless plates, melts at  $263-264^{\circ}$ , dissolves in sulphuric acid to a blue solution, forms a sparingly soluble *sodium* salt, and gives an *acetyl* derivative melting at  $126-127^{\circ}$ . The prolonged action of hydriodic acid converts the diethyl ether into 3 : 3'-*dihydroxyflavone*; this is readily soluble in alcohol, crystallises in glistening, monohydrated needles, and in the anhydrous form melts at  $277-278^{\circ}$ ; its *diacetyl* derivative melts at  $152-153^{\circ}$ . J. J. S.

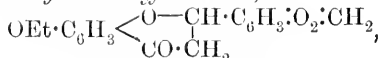
**2:3':4'-Trihydroxyflavone.** By STANISLAUS VON KOSTANECKI and TH. SCHMIDT (*Ber.*, 1900, 33, 326-330. Compare Abstr., 1899, i, 370).—3'-*Methoxy-2 : 4'-diethoxyflavanone*,



is obtained by the condensation of 3-methoxy-4-ethoxybenzaldehyde (ethylvanillin) with 2-hydroxy-5-ethoxyacetophenone in the presence of alcohol and concentrated sodium hydroxide solution; a red bye-product is formed at the same time, and can only be removed by repeated crystallisation from alcohol. It crystallises in colourless needles, melts at  $127-128^{\circ}$ , dissolves in concentrated sulphuric acid or in alcoholic potash to red solutions, and in alcohol to a pale green, fluorescent solution. By the action of bromine in carbon disulphide solution, it is converted into a *monobromo*-derivative,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ | \\ \text{CO} \end{smallmatrix} \text{C}_2\text{H}_2\text{Br} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{OEt}$ ,

which crystallises in colourless needles melting and decomposing at  $133^{\circ}$ ; strong alkali converts the bromine derivative into 3'-*methoxy-2 : 4'-diethoxyflavone*,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{OEt} \\ | \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ , which forms colourless needles melting at  $168^{\circ}$ , and soluble in alcohol to a blue, fluorescent solution.

**2-Ethoxy-3 : 4'-methylenedioxyflavanone,**



obtained from piperonal and 2-hydroxy-5-ethoxyacetophenone, crystallises in colourless needles melting at  $144^{\circ}$ ; its crude *monobromo*-derivative, when treated with alkali, yields 2-ethoxy-3 : 4'-*methylenedioxyflavone*,

melting at  $204^{\circ}$ . When heated with sodium ethoxide, these flavones are hydrolysed in exactly the same manner as other flavone derivatives (compare preceding abstract).

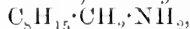
2:3':4'-*Trihydroxyflavone*, obtained when either of the above flavone derivatives is heated with concentrated hydriodic acid, forms yellowish, crystalline crusts melting and decomposing at  $328^{\circ}$ , dissolves readily in sodium hydroxide, and gives a yellow dye with alumina mordants; its *diacetyl* derivative melts at  $208-209^{\circ}$ . J. J. S.

**Formation of Flavone from its Decomposition Products.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR [with J. BONGARTZ] (*Ber.*, 1900, 33, 330—334).—The first product, obtained by the action of alkalis on flavone is *o*-hydroxybenzoylacetophenone, formed by the rupture of the  $\gamma$ -pyrone ring; this may then undergo acid hydrolysis into benzoic acid and *o*-hydroxyacetophenone, or ketonic hydrolysis into salicylic acid and acetophenone. The authors have succeeded in synthesising flavone from both of these pairs of compounds. When a mixture of ethyl *o*-ethoxybenzoate and acetophenone is treated with metallic sodium and the mixture left for 24 hours, or when a mixture of *o*-ethoxyacetophenone and ethyl benzoate is treated as recommended by Emilewicz, Kostanecki, and Tambor in the preparation of 2:4:6-trimethoxybenzoylacetophenone (*Abstr.*, 1899, i, 911), the product is *o*-ethoxybenzoylacetophenone, which, on treatment with concentrated hydriodic acid, yields flavone. J. J. S.

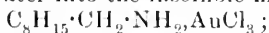
**Action of Hydroxylamine and Phenylhydrazine on Dithiobenzoylacetone.** By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1900, [iii], 23, 36—37).—Dithiobenzoylacetone,  $S_2(CHAcBz)_2$  (*Abstr.*, 1899, i, 599), reacts with hydroxylamine and phenylhydrazine to form the corresponding *oxazoledisulphide*,  $S_2(C_3ONMePh)_2$ , and *pyrazoledisulphide*,  $S_2(C_3N_2MePh)_2$ , respectively. The former crystallises from boiling alcohol in nacreous, yellow scales melting at  $91-92^{\circ}$ , whilst the latter is a crystalline, yellow powder melting at  $162^{\circ}$ . N. L.

**Conversion of Dihydrocarvone into Carvenone by means of Formic Acid.** By AUGUST KLAGES (*J. pr. Chem.*, 1899, [ii], 60, 544).—A reply to Kondakoff on a question of priority (this vol., i, 104). E. G.

**Amines containing the Camphor Nucleus.** By G. BLANC (*Compt. rend.*, 1900, 130, 38—40).—*Dihydroisolaureonamine*,



obtained quantitatively by the reduction of isolaureononitrile by sodium in presence of alcohol, is a mobile, colourless liquid boiling at  $185^{\circ}$  and of sp. gr. 0.8619 at  $15^{\circ}$ . It absorbs carbon dioxide from the air, gives the carbylamine reaction, and combines energetically with methyl iodide. The *hydrochloride* forms nacreous lamellae which melt at about  $265^{\circ}$ ; the *platinichloride*, a yellow, crystalline powder; the *aurichloride*, bright yellow needles, which melt at  $203-205^{\circ}$ , and are converted by boiling water into the insoluble modification,



the *nitrate*, nacreous leaflets which melt at  $179^{\circ}$ ; the *nitrite*, white needles stable in a hot neutral aqueous solution; the *sulphate*, white

plates melting at  $249^{\circ}$ ; the *oxalate*, slender needles melting at  $243^{\circ}$ ; the *picrate*, golden-yellow lamellae melting at  $215^{\circ}$ . All these salts decompose at their melting points.

The *benzoyl* derivative,  $C_8H_{15} \cdot CH_2 \cdot NHBz$ , forms large, striated prisms melting at  $51^{\circ}$ ; the *carbamide*,  $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot C_8H_{15}$ , slender needles melting at  $102^{\circ}$ ; the *oxamide*, transparent tablets melting at  $133$ — $134^{\circ}$ .

*Dihydroisolaureonethylamine*,  $C_8H_{15} \cdot CH_2 \cdot NHEt$ , is a colourless, mobile liquid boiling at  $205^{\circ}$ , and of sp. gr. 0.8417 at  $15^{\circ}$ . Its *nitroso*-derivative is an oily liquid; the *hydrochloride* forms nacreous plates; the *platinichloride*, orange-red needles; the *nitrite*, slender needles melting at  $161^{\circ}$ , stable in a hot neutral solution, but yielding the nitroso-derivative in presence of acids; the *sulphate* melts at  $124$ — $125^{\circ}$ , and the *picrate* at  $112$ — $114^{\circ}$ .

*Dihydroisolaureonediethylamine* boils at  $235^{\circ}$ ; its hydrochloride forms small prisms melting at  $182$ — $183^{\circ}$ , and the *platinichloride* is gummy.

*Homodihydroisolaureonamine*,  $C_8H_{15} \cdot CHMe \cdot NH_2$ , obtained by reducing the oxime of acetylisolaurelene, boils at  $190^{\circ}$ , and has a sp. gr. 0.9558 at  $15^{\circ}$ ; its hydrochloride melts and decomposes at about  $230^{\circ}$ ; the *platinichloride* is a crystalline, orange-yellow powder. C. H. B.

**Nature of Inactive Carvoxime.** By H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 160—162).—Investigation of the solidifying points of mixtures of *d*- and *l*-carvoxime leads to the conclusion that the one containing 50 per cent. of each and melting about  $20^{\circ}$  higher than either active modification, is not a racemic compound, but a pseudo-racemic mixed crystal. There is a fall of temperature between the beginning and the end of solidification, except for the mixture containing 50 per cent. of each; in no case, however, can solidification be observed corresponding with a eutectic point as would be the case were inactive carvoxime a racemic compound. Mixed crystals seem to be formed on solidification at all concentrations—a view supported by analysis of the crystals deposited.

This is the first example of a series of mixed crystals with a maximum melting point. It was found, moreover, that down to  $10^{\circ}$  no change of these mixed crystals into a racemic compound took place. J. C. P.

**Tanacetone and its Derivatives.** By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 275—277).—The ketonic acid obtained on carefully oxidising isothujone with potassium permanganate (Wallach, *Abstr.*, 1897, i, 246) boils at  $273^{\circ}$ , and is thereby converted into the keto-lactone,  $C_{10}H_{16}O_3$  (m. p.  $43^{\circ}$ ; oxime, m. p.  $155^{\circ}$ ), which is formed on oxidising thujamenthone with chromic acid; on further oxidation, the keto-lactone yields  $\beta$ -isopropylkavalinic acid, and hence probably has

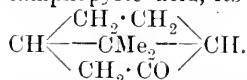
the structure  $O \begin{array}{c} \diagup \\ \text{CMeAc} \cdot \text{CHPr}^{\beta} \\ \diagdown \\ \text{CO} \end{array} \text{---} \begin{array}{c} | \\ \text{CH}_2 \end{array}$ , whilst the formulæ

$$\begin{array}{c} \text{CMe} \cdot \text{CHPr}^{\beta} \\ | \\ \text{CMe} \cdot \text{CHPr}^{\beta} \end{array} \begin{array}{c} \diagup \\ \text{CO} \end{array} \text{---} \begin{array}{c} | \\ \text{CH}_2 \end{array}, \quad \text{CHMe} \cdot \text{CHPr}^{\beta} \begin{array}{c} \diagup \\ \text{CO} \end{array} \text{---} \begin{array}{c} | \\ \text{CH}_2 \end{array},$$

and  $\text{CH}_2 \begin{array}{c} \text{CPr}^\beta - \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CHMe} \end{array} > \text{CO}$  must be given to isothujone, thujamen-thone, and tanacetone respectively.

W. A. D.

**Compounds of the Fenchone Series.** By OTTO WALLACH [with EDGARD NEUMANN and WILHELM VON WESTPHALEN] (*Chem. Centr.*, 1899, ii, 1052—1053; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—The *nitrile*,  $\text{C}_9\text{H}_{13}\text{N}$ , formed by warming the oxime of *D-d*-fenchocamphorone with dilute sulphuric acid (1 : 2), has the odours of camphonitrile and fenchonitrile and boils at 212—215°. The corresponding *acid*,  $\text{C}_8\text{H}_{13} \cdot \text{CO}_2\text{H}$ , forms a silver salt which is not affected by light. The *base*,  $\text{C}_9\text{H}_{15} \cdot \text{NH}_2$ , obtained by reducing the nitrite with alcohol and sodium, yields a carbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_9\text{H}_{15}$ , which melts at 131—132°. Since fenchocamphorone on oxidation with nitric acid forms camphopyric acid, its constitution is probably



The yellow compound,  $\text{C}_{11}\text{H}_{16}\text{O}_2$ , which melts at 96°, and is obtained by distilling lead fenchocarboxylate, forms a *dioxime*,  $\text{C}_{11}\text{H}_{16}(\text{N} \cdot \text{OH})_2$ , melting at 198—199° and soluble in water. The compound  $\text{C}_{11}\text{H}_{16}\text{O}_2$  is probably therefore an *o*-diketone or an *o*-hydroxyketone capable of acting in the tautomeric diketonic form. The pinacone,  $\text{C}_{20}\text{H}_{34}\text{O}_2$ , which melts at 122°, is also formed in the preparation of fenchocarboxylic acid. Fencholenic acid exists in two modifications. Two fencholenamides are known; the one melts at 113—114°, and the other at 85—86°. The latter corresponds with Cockburn's fencholenic acid which melts at 70°.

E. W. W.

**Oxidation of Pinene.** By OTTO WALLACH and A. SCHÄFER (*Chem. Centr.*, 1899, ii, 1052; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—The volatile compound which is formed together with  $\alpha$ -pinonic acid when pinene is oxidised by von Baeyer's method, is found to be the ketone nopinone. Nopinone is formed by the further oxidation of the small quantity of nopinic acid which von Baeyer found was always produced by the oxidation of pinene. The formation of benzylidenenopinone is in accordance with von Baeyer's theory that in nopinone the CO group is contiguous to a  $\text{CH}_2$  group.

E. W. W.

**Genesis of Terpenes in Lavender.** By EUGÈNE CHARABOT (*Compt. rend.*, 1900, 130, 257—259. Compare *Abstr.*, 1898, i, 595, and this vol., ii, 101).—An examination of three samples of essence of lavender taken from the plant at the budding, flowering, and fading stages shows that the specific gravity and optical activity of the essence increase and the amount of free acid present decreases as the plant attains maturity. The maximum quantity of esters is obtained from the plant when in flower and the amount present in the essence from the specimens with faded flowers is greater than that extracted from the young plant. The proportion of alcohol whether free or combined diminishes until the flowers have blossomed and at the same time the relative amount of esters increases; the essence from the mature

plant with faded flowers, however, contains more alcohol and less esters.

These results seem to indicate that during development the esters are produced by the direct action of the acids on the linalool and that during this period a portion of the alcohol is dehydrated; when the flowers begin to wither, esterification ceases; and then the proportion of total alcohol increases. The formation of esters and terpenes, which takes place in the green parts of the plant, is probably due to chlorophyllous evaporation. G. T. M.

**Essence of Geranium.** By JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 37—39).—Six specimens of essential oil of geranium obtained from Cannes, Spain, Corsica, Africa, Reunion, and India respectively were examined, with the following results. Sp. gr. at 15°, 0.8905—0.9073; rotation per 100 mm. at 15°,  $-0.48^\circ$  to  $-9.40^\circ$ ; acid number (mg. of KOH per 1 gram), 9.6—56.0; saponification number, 43.0—74.0; esters as  $C_{12}H_{20}O_2$ , 6.65—11.30 per cent.; alcohols as  $C_{10}H_{18}O$ , 61.31—84.62 per cent. All the samples contained free acid, the amount of which was increased by exposure to the air. The solubility of the oils in alcohol was nearly constant, 1 vol. being dissolved by 0.9—1.0 vol. of 80 per cent. alcohol, or 2—2.3 vols. of 70 per cent. alcohol, at 15°. N. L.

**Composition of East Indian Essence of Sandalwood.** By M. GUERBET (*Compt. rend.*, 1900, 130, 417—420).—A specimen of essence of sandalwood from Bombay was of a pale yellow colour and oily consistence, and had a sp. gr. 0.9684 at 0° and a rotatory power  $[\alpha]_D -21.1^\circ$ . It contained 90.1 per cent. of alcohols calculated as  $C_{15}H_{26}O$ , and esters corresponding with 7 mg. of potassium hydroxide per 1 gram of the oil; no free acid or base was detected. The following compounds were isolated from the essence: (1) Two isomeric sesquiterpenes:  *$\alpha$ -santalene*, boiling at  $252-252.5^\circ$  and having a sp. gr. 0.9134 at 0° and a rotatory power  $[\alpha]_D -13.98^\circ$ , and  *$\beta$ -santalene* boiling at  $261-262^\circ$  and having a sp. gr. 0.9139 at 0° and a rotatory power  $[\alpha]_D -28.55^\circ$ ; both are colourless, oily liquids of feeble odour.  *$\beta$ -Santalene* has previously been isolated by Soden and Müller (*Pharm. Zeit.*, 44, 258). (2) A mixture of alcohols,  $C_{15}H_{26}O$ , distilling at  $183-197^\circ$  under 37 mm. pressure and having rotatory powers ranging from  $[\alpha]_D -9.4^\circ$  to  $[\alpha]_D -25.3^\circ$ ; this probably consists of  *$\alpha$ -* and  *$\beta$ -santalols*, corresponding with  *$\alpha$ -* and  *$\beta$ -santalene*. (3) An aldehyde, *santalal*,  $C_{15}H_{24}O$ , a colourless, oily liquid of strong pepper-like odour and boiling at  $180^\circ$  under 40 mm. pressure; it forms a *semicarbazone* which crystallises in small needles melting at  $212^\circ$ . (4) *Santalalic acid*,  $C_{15}H_{24}O_2$ , a colourless, viscous liquid which boils at  $210-212^\circ$  under 20 mm. pressure and is insoluble in water; the *potassium*, *sodium*, and *barium* salts are crystalline compounds which are decomposed by carbon dioxide. This acid is also formed when *santalal* is oxidised with chromic acid in acetic acid solution. (5) *Teresantalic acid*,  $C_{10}H_{14}O_2$ , crystallises from alcohol in large, colourless prisms melting at  $157^\circ$  and boiling at  $183^\circ$  under 28 mm. pressure. The *potassium* salt was obtained as a nacreous, crystalline mass; the *calcium* salt crystallises with  $2H_2O$ . (6) 0.2—0.3 per cent. of odorous substances,



which could not be obtained in the pure state ; small quantities of acetic and formic acids were also found.

N. L.

**Curangin, the Glucoside of *Curanga amara*.** By S. E. BOORSMA (*Chem. Centr.*, 1899, ii, 991—992, 1125 ; from *Ned. Tijds. Pharm.*, 11, 303—316, 327—336. Compare *Mededeel. nits'-Land-Plantentuin*, 18).—The bitter febrifuge curangin,  $C_{48}H_{77}O_{20}$ , may be extracted from the *Scrophulariaceae* by means of ethyl acetate. This glucoside is easily soluble in ethyl or methyl alcohol, or in acetone or ethyl acetate containing water ; 100 parts of water dissolve 0.18 part. The solutions are neutral. When heated at  $100^{\circ}$ , curangin loses 7—10 per cent. of water, but the residue regains this amount on exposure to air. Its colour reactions, &c., are described in detail. By the action of benzoyl chloride and sodium hydroxide solution, it forms a compound,  $C_{48}H_{69}O_{20}Bz_8$ , which melts at  $128^{\circ}$ , and with phenylhydrazine it yields a compound which contains nitrogen and melts at  $163^{\circ}$ . Attempts to prepare a bromide failed, as the hydrogen bromide which is formed decomposes the glucoside. When curangin is boiled with a 2 per cent. solution of hydrogen chloride in alcohol, it is decomposed into *curangaegenin* and a sugar, which appears to consist mainly of rhamnose. The crude curangaegenin contains two compounds, of which the one (A) present in the larger quantity, is soluble in ether, and is apparently partially converted into the other (B) by prolonged boiling with the alcoholic acid solution ; (B) is insoluble in ether. Both substances are easily soluble in ethyl acetate, acetone, glacial acetic acid, or methyl, ethyl, or amyl alcohol. Their colour reactions are given in detail.

E. W. W.

**Arrow Poison of Wakamba (German East Africa).** By LUDWIG BRIEGER (*Chem. Centr.*, 1899, ii, 1130 ; from *Deutsch. med. Woch.*, 25, No. 39).—The Wakamba arrow poison is a glucoside,  $C_{26}H_{46}O_{19}$ , and somewhat resembles Arnaud's ouabain (*Abstr.*, 1888, 848). It crystallises from a hot saturated solution in anhydrous needles which melt at  $182$ — $184^{\circ}$ , but the plates obtained by allowing the compound to crystallise more slowly contain 20 per cent. of water and melt at  $93$ — $94^{\circ}$ . It is insoluble in ether, ethyl acetate, chloroform, or benzene, slightly soluble in cold water, and more easily soluble in hot water or alcohol. The specific rotatory power for a 4 per cent. aqueous solution is  $[\alpha]_D -37^{\circ}$ . When the compound is boiled with dilute hydrochloric or sulphuric acid, a yellow, amorphous precipitate is formed ; this is easily soluble in alcohol, and is not poisonous. The filtrate reduces Fehling's solution, although the poison itself is incapable of doing so. The filtrate may also be fermented, and yields an amorphous glucosazone. The aqueous solution of the glucoside does not give precipitates with the ordinary alkaloidal reagents. A dose of 0.3 mg. per kilogram of body weight proved fatal in the case of dogs in 2 hours.

An amorphous, non-poisonous substance was also isolated.

E. W. W.

**Chlorophyll.** By LEO MARCHLEWSKI (*J. pr. Chem.*, 1900, 61, 47—63).—A continuation of the controversy with Bode (*Abstr.*, 1898, i, 682 ; this vol., i, 109) and Kohl (*Bot. Centr.*, 1899, 233).

T. M. L.

**New Method of Methylation.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1900, [iii], 23, 69—71).—The methylation of amino-groups in certain leuco-bases and colouring matters is readily effected by heating a solution of the substance with zinc dust, hydrochloric acid, and formaldehyde at 75—80°, the decolorised liquid being subsequently oxidised either by exposure to air, or by lead peroxide and acetic acid. Details are given of the application of this process to the production of methyl-violet from magenta, of a methylated rhodamine derived from *m*-diaminophenol, of methylene-blue and a greenish-blue dye from thionine, and of blue and violet colouring matters from phenosafranine. N. L.

**Reactions of Methylfurfuraldehyde and Methylpentosans.** By JOHN A. WIDTSOE and BERNHARD TOLLENS (*Ber.*, 1900, 33, 143—148. Compare Andrlík, this vol., i, 110).—The colour reactions of furfuraldehyde are masked in the presence of methylfurfuraldehyde. The latter is readily detected by the characteristic spectrum exhibited in the presence of hydrochloric acid. Several vegetable products, when distilled with hydrochloric acid, yield a distillate, which, when mixed with an equal volume of concentrated hydrochloric acid, shows this spectrum. Among these are : tragacanth, gum arabic, gedda gum, Brazil gum, cherry gum, *Fucus*, plane and lime tree leaves, and turf-mould. R. H. P.

**Ketones of the Tropine Group. XIII. Hydroxymethylenetropinone.** By RICHARD WILLSTÄTTER and FRITZ IGLAUER (*Ber.*, 1900, 33, 359—365. Compare Abstr., 1899, i, 178).—*Hydroxy-*

$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{C} \cdot \text{CH} \cdot \text{OH} \\ | \quad | \\ \text{NMe} \quad \text{CO} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \end{array}$$

*methylenetropinone*, prepared by heating tropinone

in dry ether with amyl formate and sodium ethoxide, crystallises in aggregates of colourless plates, and melts at 128—128.5°, when it decomposes ; the aqueous and alcoholic solutions develop an intense reddish-violet coloration with ferric chloride, and reduce Fehling's solution when heated. The aqueous solution is neutral to litmus and turmeric, forming unstable salts with acids and alkalis ; the silver, gold, and platinum derivatives are indefinite, and readily decomposed. Digestion with alkalis or mineral acids eliminates formic acid. Precipitates are formed with phosphomolybdic acid, iodine in potassium iodide, or tannin ; the *picrate* is sparingly soluble in cold water, and melts at 177°, when it decomposes. The *anilide* crystallises from alcohol in aggregates of colourless needles, and melts at 158°. The compound,  $\text{C}_9\text{H}_{15}\text{O}_2\text{N}_2\text{Cl}$ , prepared by the action of hydroxylamine, followed by alcoholic hydrogen chloride, on hydroxymethylenetropinone, crystallises from alcohol in lustrous leaflets and melts at 239°, when it decomposes ; water dissolves it very readily, and the liquid reduces Fehling's solution, and develops a dark green coloration with ferric chloride.

Tropinone combines with ethyl acetate in presence of sodium ethoxide, forming acetyltropinone, the *platinichloride* of which is crystalline.

*Tropinonesemicarbazone*,  $C_9H_{16}ON_4$ , crystallises from alcohol in long, six-sided plates, and melts at  $212-213^\circ$ . M. O. F.

**Ketones of the Tropine Group. XIV. Alkali-salts of Amino-ketones.** By RICHARD WILLSTÄTTER and ADOLF BODE (*Ber.*, 1900, 33, 411—416).—When dissolved in ether or benzene, tropinone is gradually acted on by sodium or potassium, giving a metallic salt which separates as a pale yellow powder, and is completely hydrolysed by water. If stick potash is dried by heating and cooled to  $130-160^\circ$ , it combines completely with a tenth of its weight of fused tropinone, and the latter cannot be detected either by its smell or by turmeric paper, but is separated completely by adding water. A certain amount of a salt is also produced when an ethereal solution of tropinone is dried with stick potash or soda; a further decomposition also occurs, tropic acid being produced. Triacetoneamine, *N*-methylgranatonine (pseudopelletierine), and dimethylaminosuberone behave similarly.

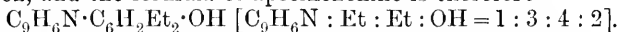
When oxidised with chromic acid, *l*-ecgonine gives inactive tropinone, although in the oxidation to tropic acid both *d*- and *l*-ecgonine give *d*-tropic acid; this is readily explained if the formation of an active intermediate,  $\beta$ -ketonic acid, 
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{NMe} \quad \text{CO} \end{array}$$
, be assumed, since 
$$\text{CH}_2 \cdot \text{CH} - \text{CH} \cdot \text{CO}_2\text{H}$$
 this would give an inactive tropinone by losing a mol. of carbon dioxide, but an active tropic acid by further oxidation. T. M. L.

**Conversion of Cinchona-alkaloids into Derivatives of 4-Phenylquinoline** By WILHELM KOENIGS (*J. pr. Chem.*, 1900, 61, 1—46. Compare Comstock and Koenigs, *Abstr.*, 1892, 1010).—*Nitroapocinchenine*,  $C_{19}H_{15}ON \cdot NO_2$ , prepared by the action of nitrous acid on apocinchenine, crystallises from dilute alcohol in colourless needles, and melts with decomposition at  $228^\circ$ ; it does not give Liebermann's reaction. The *platinichloride*,  $(C_{19}H_{15}O_3N_2)_2 \cdot H_2PtCl_6$ , is an orange-yellow, crystalline powder, and is readily decomposed by water. The *ethyl ether*, prepared by the action of ethyl iodide on the insoluble silver salt, crystallises from alcohol in yellow tablets and melts at about  $124^\circ$ ; it is reduced by tin and hydrochloric acid to the corresponding *amino-ether*, which is readily soluble in alcohol and ether, and forms a *sulphate* which crystallises from hot water in golden-yellow flakes, but dissolves again in an excess of dilute sulphuric acid.

*Aminoapocinchenine*,  $C_{19}H_{15}ON \cdot NH_2$ , prepared by reducing the nitro-compound, crystallises from alcohol in almost colourless needles and melts at  $220^\circ$ ; it forms two series of salts, red salts with dilute acetic acid or a small amount of dilute mineral acid, and yellow salts with an excess of mineral acid. Chromic acid oxidises the base to cinechonic acid, showing that the amino-group is in the phenyl, and not in the quinoline, nucleus; in presence of dilute sulphuric acid, lead peroxide oxidises it to an intensely red solution, which becomes yellow again on adding sulphurous acid; these compounds appear to be the quinone and quinol corresponding with the original aminophenol, and the amino-group is therefore in the para-position to the hydroxyl group;

the quinol, *hydroxyapocinchenine*, was isolated in pale yellow crystals melting at  $251^{\circ}$ , but was not analysed.

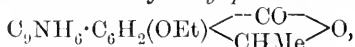
It has already been shown that the hydroxyl group in apocinchenine is adjacent to the quinoline radicle, and that the two ethyl groups occupy adjacent positions; its behaviour towards nitrous acid shows that the para-position to the hydroxyl group is occupied by hydrogen, and the formula of apocinchenine is therefore



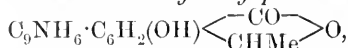
A second *nitroapocinchenine* is produced by the action of nitric acid on apocinchenine; the *hydrochloride* crystallises from hot water in colourless, glistening flakes, with  $3\text{H}_2\text{O}$ , and melts and decomposes at  $150\text{--}160^{\circ}$ ; the *nitrate* and *sulphate* are also crystalline.

*Tetrahydroapocinchenine*,  $\text{C}_{19}\text{H}_{23}\text{ON}$ , prepared by reducing apocinchenine with tin and hydrochloric acid, forms a yellow, soluble resin. *Diacetyltetrahydroapocinchenine*,  $\text{C}_{19}\text{H}_{21}\text{NAc}\cdot\text{OAc}$ , crystallises from alcohol in colourless needles, melts at  $133\text{--}135^{\circ}$ , and is readily hydrolysed by alcoholic potash or by alcoholic hydrogen bromide. Homoapocinchenine and apoquinine can be similarly reduced.

In the oxidation of apocinchenine ethyl ether with dilute nitric acid there is produced, in addition to apocinchenic acid ethyl ether, a basic compound,  $\text{C}_9\text{H}_6\text{N}\cdot\text{CHO}$ , which crystallises from hot water in colourless needles and melts at  $101\text{--}102^{\circ}$ ; this is oxidised by ammoniacal silver oxide to cinchoninic acid, and is therefore 4-quinolinealdehyde; the *platinichloride* is a crystalline, orange-yellow powder. The oxidation of apocinchenine ethyl ether by manganese dioxide or lead peroxide and dilute sulphuric acid gives ketoapocinchenine ethyl ether, apocinchenic acid ethyl ether, and the lactone of hydroxyapocinchenic acid ethyl ether. *Ketoapocinchenine ethyl ether*,  $\text{C}_9\text{NH}_6\cdot\text{C}_6\text{H}_2\text{Et}(\text{OEt})\cdot\text{COMe}$ , crystallises from a mixture of ether and light petroleum and melts at  $104\text{--}106^{\circ}$ ; the *platinichloride* crystallises in minute, felted needles; the *oxime* is crystalline, melts at  $181\text{--}184^{\circ}$ , and dissolves in dilute sodium hydroxide, but is reprecipitated by carbon dioxide; by heating with concentrated hydrobromic acid, the ketone is converted into homoapocinchenine,  $\text{C}_9\text{NH}_6\cdot\text{C}_6\text{H}_3\text{Et}\cdot\text{OH}$ , together with acetic acid and ethyl bromide. The *lactone* of *hydroxyapocinchenic acid ethyl ether*,



which is also produced by oxidising apocinchenic acid ethyl ether with manganese dioxide and sulphuric acid, separates from methyl or ethyl alcohol in colourless crystals and melts at  $212\text{--}213^{\circ}$ ; hydrobromic acid converts it into the *lactone* of *hydroxyapocinchenic acid*,



which crystallises in colourless, felted needles, sinters at  $260^{\circ}$ , melts about  $274^{\circ}$ , dissolves in cold caustic alkalis, and is reprecipitated by carbon dioxide, but is hydrolysed by boiling with alkalis; hydriodic acid converts it into homoapocinchenine,  $\text{C}_9\text{NH}_6\cdot\text{C}_6\text{H}_3\text{Et}\cdot\text{OH}$ , carbon dioxide, and ethyl iodide, thus providing the best method for preparing homoapocinchenine; chromic acid oxidises it to cinchoninic acid; a solution of bromine in an excess of sodium hydroxide converts it almost quantitatively into quinolinephenetoleldicarboxylic acid and

carbon tetrabromide; nitric acid, alkaline permanganate, and iodine only oxidise it with difficulty. *Quinolinephenetoleedicarboxylic acid*,  $C_9NH_6 \cdot C_6H_3(CO_2H)_2 \cdot OEt$ , separates from alcohol in colourless crystals, melts at  $236^\circ$  with evolution of gas, and is only slightly soluble in water; the *hydrochloride* is completely decomposed by boiling water; the *anhydride* crystallises from ethyl acetate in minute, colourless, felted needles, melts at  $210-211^\circ$ , and gives a fluorescein when fused with resorcinol; chromic acid oxidises the acid to cinchoninic acid, whilst concentrated hydrobromic acid converts it into homoapocinchenic acid,  $C_9NH_6 \cdot C_6H_3(OH) \cdot CO_2H$ ; the silver salt loses carbon dioxide when heated to  $280-290^\circ$  and gives a small amount of phenetolequinoline,  $C_9NH_6 \cdot C_6H_4 \cdot OEt$ .

The oxidation of homoapocinchenine ethyl ether,  $C_9NH_6 \cdot C_6H_3Et \cdot OEt$ , with nitric acid gives an acid melting at  $236^\circ$ , together with a base which crystallises from dilute alcohol in white, felted needles, melts at  $118^\circ$ , and is found to be a *nitro*-derivative. Oxidation with manganese dioxide or lead peroxide and sulphuric acid gives ketoapocinchenine ethyl ether, homoapocinchenic acid ethyl ether, and some cinchonic acid. *Ketohomoapocinchenine ethyl ether*,  $C_9NH_6 \cdot C_6H_3(OEt) \cdot COMe$ , separates from ether in colourless crystals and melts at  $107-109^\circ$ ; the *platinichloride* crystallises in long, reddish-yellow needles and melts and decomposes at  $248^\circ$ . The *phenylhydrazone* separates from hot alcohol in pale yellowish crystals and melts at  $220^\circ$ . Iodine in presence of potassium carbonate converts the ketone partially into iodoform and homoapocinchenic acid ethyl ether, but the oxidation proceeds quantitatively when sodium hypobromite is used. *Homoapocinchenic acid ethyl ether*,  $C_9NH_6 \cdot C_6H_3(OEt) \cdot CO_2H$ , crystallises from alcohol, melts at  $253-254^\circ$ , and is only slightly soluble in water, but dissolves in hot dilute mineral acids. The *sulphate* and *platinichloride* are crystalline; hydrogen bromide converts the acid into homoapocinchenic acid, but unlike the homologue it does not lose carbon dioxide. *Homoapocinchenic acid*,  $C_9NH_6 \cdot C_6H_3(OH) \cdot CO_2H$ , which is also produced from quinoline phenetoleedicarboxylic acid by prolonged boiling with hydrobromic acid, is obtained as a colourless, flocculent, slightly soluble precipitate, and does not melt at  $290^\circ$ . On heating the silver salt with zinc dust, it is converted into phenolquinoline.

*Quinolinephenetole*,  $C_9NH_6 \cdot C_6H_4 \cdot OEt$ , crystallises from dilute alcohol in colourless needles and melts at  $80-81^\circ$ . The *picrate* melts at  $201-202^\circ$ . *Quinolinephenol*,  $C_9NH_6 \cdot C_6H_4 \cdot OH$ , crystallises from alcohol and melts at  $207-208^\circ$ ; the *hydrochloride* melts at  $260^\circ$ , and the *hydrobromide* at  $274^\circ$ .

*6-Aminoapocinchenine*,  $NH_2 \cdot C_9NH_5 \cdot C_6H_3Et_2 \cdot OH$ , prepared by heating apocinchenine with zinc ammonium chloride, crystallises from alcohol and melts at  $229-230^\circ$ . The *hydrochloride* forms golden yellow crystals. *6-Aminoapocinchenine ethyl ether*,  $NH_2 \cdot C_9NH_5 \cdot C_6H_3Et_2 \cdot OEt$ , crystallises from dilute alcohol and melts at  $148-150^\circ$ ; by the action of copper powder on the diazo-compound, the base is converted into apocinchenine.

Dihydrocinchenine (Abstr., 1894, i, 392, 629) differs entirely from cinchenine in that it is not acted on by hydrobromic acid; it crystallises from dilute methyl alcohol and melts at  $145^\circ$ ; the *platinichloride*

crystallises from dilute hydrochloric acid in yellowish-red, microscopic tablets and melts at  $265^{\circ}$ ; the *picrate* melts at  $197^{\circ}$ . When heated with phosphoric acid, it is hydrolysed like cinchenine, but gives cincholeupone,  $C_9H_{17}NO_2$ , in place of meroquinine,  $C_9H_{15}NO_2$ , together with lepidine.

T. M. L.

**Non-nitrogenous Decomposition Products of Morphine.**  
 VI. By EDUARD VONGERICHTEN (*Ber.*, 1900, **33**, 352—359. Compare Abstr., 1899, i, 649).—As a result of oxidising acetylmorphenol, the author has been led to modify his expressions for the constitution of morphenol and morphol, and now represents these compounds by the formulae  $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_3 \\ \text{CH} \cdot \text{C}_6\text{H}_2(\text{OH}) \end{array} \text{>O}$  and  $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_4 \\ \text{CH} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \end{array}$  [OH : OH : CH = 2 : 3 : 6] respectively. He considers that the constitution of morphine is expressed by the formula advocated by Knorr (Abstr., 1899, i, 464).

When acetylmorphenol is oxidised with chromic acid, a quinone is produced which combines with *o*-tolylenediamine, forming the *azine*,  $C_{23}H_{14}O_3N_2$ , crystallising from glacial acetic acid in small, yellow needles melting at  $231$ — $232^{\circ}$ ; hydrochloric acid develops a bright red coloration with the *azine*, which forms an intensely blue solution in concentrated sulphuric acid.

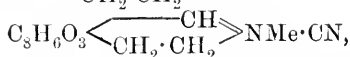
*Benzoylmorphenol*,  $C_{21}H_{12}O_3$ , crystallises from glacial acetic acid in small, colourless aggregates, and melts at  $123^{\circ}$ . *Bromoacetylmorphenol*,  $C_{16}H_9O_3Br$ , melts at  $208^{\circ}$ .

A method is described by which morphenol can be prepared from morphine in yield amounting to nearly 40 per cent. of the calculated quantity.

M. O. F.

**Cotarnine.** By MARTIN FREUND [and HUGO PREUSS] (*Ber.*, 1900, **33**, 380—389. Compare Hantzsch and Kalb, this vol., i, 115).—

*Cyanocotarnine*,  $C_8H_6O_3 \left\langle \begin{array}{c} \text{CH}(\text{CN}) \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle \text{NMe}$ , or



prepared by the action of aqueous hydrogen cyanide on cotarnine, crystallises from alcohol in prisms which melt at  $95$ — $96^{\circ}$ ; aqueous acids eliminate hydrogen cyanide, and a solution of hydrogen chloride in benzene regenerates cotarnine hydrochloride. Contrary to Hantzsch and Kalb's statement, silver nitrate and silver oxide give rise to silver cyanide. The *methiodide*,  $C_{11}H_{17}O_3N_2I$ , crystallises from hot water and melts at  $204$ — $205^{\circ}$ , when it decomposes.

*Cotarnine sulphide*,  $C_{24}H_{25}O_6N_2S$ , obtained on passing hydrogen sulphide into a concentrated solution of cotarnine in absolute alcohol, dissolves sparingly in benzene or alcohol, being almost insoluble in ether or petroleum; it melts and decomposes at  $146$ — $148^{\circ}$ . The substance is indifferent towards aqueous alkalis and alcoholic potash, but dilute acids eliminate hydrogen sulphide and regenerate cotarnine, whilst methyl iodide in hot chloroform gives rise to mercaptan and cotarnine hydriodide.

*Cotarnine peroxide*,  $C_{21}H_{23}O_8N_2$ , prepared by treating a saturated

solution of cotarnine in methyl alcohol with hydrogen peroxide, melts and intumesces at  $140^{\circ}$ ; it liberates iodine from potassium iodide, and acids eliminate hydrogen peroxide. Methyl iodide gives rise to cotarnomethine methiodide, and acetic anhydride converts it into acetyl hydrocotarnineacetic acid (Bowman, Abstr., 1887, 1056).

M. O. F.

**Action of Halogens on Dimethylpiperidine.** By RICHARD WILLSTÄTTER (*Ber.*, 1900, 33, 365—379. Compare Ladenburg, Abstr., 1882, 534, and Merling, Abstr., 1884, 1385).—2-Iodomethyl-1:1-dimethylpyrrolidinium iodide,  $\text{CH}_2\text{I}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\text{---CH}_2 \\ \text{NMe}_2\text{I}\cdot\text{CH}_2 \end{smallmatrix}$ , prepared by

heating alcoholic dimethylpiperidine with iodine, crystallises from water in long, snow-white prisms, which melt and decompose at  $211\text{--}212^{\circ}$ ; it is precipitated from aqueous solutions by caustic soda. The bromine

compound,  $\text{CH}_2\text{Br}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\text{---CH}_2 \\ \text{NMe}_2\text{Br}\cdot\text{CH}_2 \end{smallmatrix}$ , crystallises from alcohol in small, four-sided plates or short prisms, and melts, evolving gas, at about  $232^{\circ}$ . Although hitherto regarded as derivatives of dimethylpiperidine, these compounds are really derived from pyrrolidine. 2-Bromomethyl-1:1-di-

methylpyrrolidinium chloride,  $\text{CH}_2\text{Br}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\text{---CH}_2 \\ \text{NMe}_2\text{Cl}\cdot\text{CH}_2 \end{smallmatrix}$ , obtained from the preceding compound and silver chloride, crystallises from alcohol in lustrous prisms, which melt and decompose at  $224\text{--}225^{\circ}$ ; the *iodide* separates from water in four-sided plates, and melts at  $218\text{--}219^{\circ}$ .

When the bromo-bromide and iodo-iodide are heated with caustic alkalis, halogen hydride is removed, and salts of 1:1-dimethyl-2-methylenepyrrolidinium hydroxide,  $\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}_2\text{---CH}_2 \\ \text{NMe}_2(\text{OH})\cdot\text{CH}_2 \end{smallmatrix}$ , are produced.

The *iodide* is excessively soluble in cold water, and crystallises from alcohol in long, transparent prisms, which melt and decompose at  $196^{\circ}$ ; the *bromide* forms small, hygroscopic needles, and the *chloride* is deliquescent. The *platinichloride* separates from water in orange-red prisms, and gradually decomposes at about  $210^{\circ}$ ; the *aurichloride* crystallises from hot water in golden-yellow, microscopic prisms which melt and decompose at  $226\text{--}227^{\circ}$ .

Reduction of iodomethyldimethylpyrrolidinium iodide with zinc and concentrated hydriodic acid gives rise to 1:2-dimethylpyrrolidine methiodide (Fenner and Tafel, Abstr., 1898, i, 446). Agitating aqueous solutions of the bromo-bromide and iodo-iodide with zinc dust regenerates the base.

On reducing 1:1-dimethyl-2-methylenepyrrolidinium iodide with tin and hydrochloric acid, an isomeric *iodide*,  $\text{C}_7\text{H}_{11}\text{NI}$ , is produced, which is also unsaturated; it crystallises in thin, white, lustrous leaflets, which melt and decompose at  $232^{\circ}$ . The *platinichloride* and *aurichloride* melt at  $210^{\circ}$  and  $256^{\circ}$  respectively.

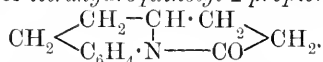
M. O. F.

**Optical Properties of Granatan- and Tropane-nuclei.** By ANTONIO PICCININI (*Real. Accad. Lincei.*, 1899, [v], 8, ii, 219—222).—The

inactive base methylgranatonine,  $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \\ \text{NMe} \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CO}$ , must be

regarded as internally compensated, since, according to van't Hoff's theory, the two asymmetric carbon atoms joined to the nitrogen cannot both have a + or both a - rotation without considerable deformation of the nucleus. When the oxygen atom is replaced by  $\text{H}_2$  and the Me by H, granatanine is obtained, and the molecule contains no asymmetric carbon atom. Similarly, tropine and  $\psi$ -tropine are seen to be internally compensated, as also are all their derivatives the molecules of which retain intact the tropine nucleus and have two equivalent asymmetric carbon atoms. T. H. P.

**Tetrahydroquinolyl-2-propionic Acid.** By WILHELM KOENIGS (*Ber.*, 1900, 33, 218—228).—The substance obtained by Einhorn and Sherman (*Abstr.*, 1896, i, 61) by the reduction of quinolyl-2-acrylic acid, and described by them as  $\alpha$ -quinolylpropyl alcohol, is in reality the inner anhydride of tetrahydroquinolyl-2-propionic acid,



The corresponding acid,  $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is best prepared by reducing quinolylacrylic acid with sodium and alcohol, but has not been obtained crystalline; it dissolves readily in water or acids, yielding solutions which give a dark red coloration with ferric chloride or potassium dichromate. The sodium, barium, and calcium salts are readily soluble but do not crystallise, whilst the copper salt is an amorphous precipitate. When the solution of the acid is warmed, the anhydride is formed, which is only very sparingly soluble in water, and melts at 115—116°. Boiling aqueous alkalis only decompose the anhydride very slowly, a salt of the acid being produced. The anhydride gives a violet coloration with sulphuric acid and potassium dichromate, similar to that produced by strychnine, to which it is apparently closely related in constitution. When the powdered anhydride, suspended in water, is injected into a frog, no perceptible physiological action occurs.

*Nitrosotetrahydroquinolyl-2-propionic acid,*



is prepared from the sodium salt of the acid, and crystallises in lustrous prisms which melt and decompose at 116—117°; it forms crystalline salts, gives Liebermann's reaction, and does not yield an anhydride.

The investigation is being extended to other acids such as quinolyl-4-acrylic acid, which appears to yield a tetrahydro-derivative on reduction, but does not readily form an anhydride. A. H.

***as*-Phenylhydrazine Derivatives.** By HANS RUPE and HANS LABHARDT (*Ber.*, 1900, 33, 246—249. Compare this vol., i, 258).— $\alpha$ -Acetyl- $\beta$ - $\delta\delta$ -triphenylsemicarbazide,  $\text{NHAc} \cdot \text{NPh} \cdot \text{CO} \cdot \text{NPh}_2$ , obtained by heating diphenylcarbamic chloride and  $\beta$ -acetylphenylhydrazine in boiling cumene, separates from aromatic hydrocarbon solutions in well-defined, flattened crystals.



*βδδ-Triphenylsemicarbazide*,  $\text{NH}_2 \cdot \text{NPh} \cdot \text{CO} \cdot \text{NPh}_2$ , is produced by heating the preceding compound with dilute sulphuric acid and alcohol and decomposing the resulting sulphate with sodium carbonate; the free base forms colourless crystals, and melts at  $128^\circ$ : the *sulphate* melts at  $98^\circ$ ; the *benzylidene* derivative,  $\text{CHPh} \cdot \text{N} \cdot \text{NPh} \cdot \text{CO} \cdot \text{NPh}_2$  forms colourless needles and melts at  $160$ – $161^\circ$ . G. T. M.

**Phenylethylenehydrazine.** By M. HIRSCHMANN (*Annalen*, 1899, 310, 156–164. Compare Burchard and Michaelis, *Abstr.*, 1890, 250).—*Ethylenebisdiphenylsemicarbazide*,  $\text{C}_2\text{H}_4(\text{NPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{NPh})_2$ , prepared from phenylethylenehydrazine and excess of phenylcarbimide, is sparingly soluble in organic media, but crystallises from boiling alcohol in small prisms melting at  $207$ – $208^\circ$ . *Ethylenebisphenylsemicarbazide*,  $\text{C}_2\text{H}_4(\text{NPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$ , obtained from potassium cyanate and phenylethylenehydrazine hydrochloride, melts at  $237.5^\circ$ , and forms a crystalline *acetate* which dissociates below its melting point.

*Ethyl ethylenebisphenylcarbazinate*,  $\text{C}_2\text{H}_4(\text{NPh} \cdot \text{NH} \cdot \text{CO}_2\text{Et})_2$ , produced by the action of ethylic chlorocarbonate on phenylethylenehydrazine, separates from alcohol in small crystals and melts at  $170$ – $171^\circ$ . The *methyl* ester forms lustrous leaflets and melts at  $176$ – $177^\circ$ .

*Ethylenecarbonylbisphenylhydrazide*,  $\text{C}_2\text{H}_4 \left\langle \begin{smallmatrix} \text{NPh} \cdot \text{NH} \\ \text{NPh} \cdot \text{NH} \end{smallmatrix} \right\rangle \text{CO}$ , obtained from carbonyl dichloride and phenylethylenehydrazine, crystallises from alcohol in lustrous, colourless needles and melts at  $199$ – $200^\circ$ .

*Ethylenebisphenylpicrazide*,  $\text{C}_2\text{H}_4[\text{NPh} \cdot \text{NH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3]_2$ , prepared from picryl chloride and phenylethylenehydrazine, melts at  $202.5^\circ$ , when it blackens and intumescs. *Phenylhydrazinephenylethylenepicrazide*,  $\text{NH}_2\text{Ph} \cdot \text{N} \cdot \text{C}_2\text{H}_4 \cdot \text{NPh} \cdot \text{NH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$ , is a by-product in the preparation of the foregoing substance and melts at  $152^\circ$ , forming a *hydrochloride* which contains  $4\frac{1}{2}\text{H}_2\text{O}$ , and melts at  $165$ – $166^\circ$ , when it decomposes. The *sulphate* and *nitrate* melt at  $127$ – $128^\circ$  and  $120$ – $121^\circ$  respectively. M. O. F.

**New Aldazines and their Behaviour towards Benzoyl Chloride.** By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 467–477).—*Dibenzoyl-o-benzylideneazaine*,



prepared by the action of benzoyl chloride on dihydroxy-*o*-benzylideneazaine, crystallises from benzene in glistening, yellow needles melting at  $188$ – $189^\circ$ .

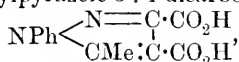
*m*- and *p*-*Nitrobenzylideneazaine*,  $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , obtained by the interaction of nitrobenzaldehyde and hydrazine sulphate, crystallises from benzene in glistening, yellow plates; the meta-compound melts at  $194$ – $195.5^\circ$ , whilst the para-form does not fuse at  $260^\circ$ .

T. H. P.

**Replacement of the Aldehyde Group  $\text{R} \cdot \text{CH} \cdot$  by Benzoyl in Hydrazine Derivatives.** By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 377–386).—According to the conditions of experiment, the reaction between furfurylideneazaine and benzoyl chloride

gives rise to three different substances: symmetrical dibenzoylhydrazine, benzoylbenzylidenehydrazine, and *furfurylidenebenzoylhydrazine*,  $C_4H_3O \cdot CH:N \cdot NHBz$ , which separates from alcohol in yellowish, flattened needles melting at  $178-179^\circ$ . T. H. P.

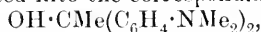
**So-called Isopyrazole Derivatives.** By FRIEDRICH STOLZ (*Ber.* 1900, 33, 262—265. Compare this vol., i, 56).—On heating Bülow and Schlesinger's "1-phenyl-3-methylisopyrazole-4:5-dicarboxylic acid," carbon dioxide is evolved and Claisen's 1-phenyl-5-methylpyrazole-4-carboxylic acid,  $CO_2H \cdot C \begin{smallmatrix} \swarrow CMe \cdot NPh \\ \searrow CH=N \end{smallmatrix}$ , is obtained (Abstr., 1894, i, 345, and 1897, i, 440); this indicates that the dicarboxylic acid is in reality 1-phenyl-5-methylpyrazole-3:4-dicarboxylic acid,



and therefore "1-phenyl-3-methylisopyrazole" is identical with 1-phenyl-5-methylpyrazole.

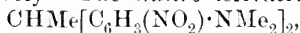
The discrepancy existing between the melting point of Knorr and Laubmann's dicarboxylic acid (m. p.  $198^\circ$ , Abstr., 1889, 409) and that of Bülow and Schlesinger's acid (m. p.  $247^\circ$ ) is due to the presence of an isomeride in the former preparation, the substance being obtained by the oxidation of 1-phenyl-3:5-dimethylpyrazole-4-carboxylic acid, a process which might give rise to two dicarboxylic acids according as to which of the methyl groups undergoes oxidation. The *acid ester*,  $C_{14}H_{14}N_2O_4$ , the first product of the hydrolysis of diethyl benzeneazodiacetylsuccinate, crystallises from alcohol in needles and melts at  $185^\circ$ ; on further treatment with alcoholic sulphuric acid, this compound yields the free dicarboxylic acid (m. p.  $247^\circ$ ). G. T. M.

**Derivatives of the Leuco-base,  $C_{18}H_{24}N_2$ .** By AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1899, [iii], 23, 20—24. Compare Abstr., 1899, i, 615).—When *as*-tetramethyldiaminodiphenylethane,  $CHMe(C_6H_4 \cdot NMe_2)_2$ , is dissolved in anhydrous acetic acid and treated with lead peroxide in the cold, it is converted into the corresponding *carbinol*,



which was obtained as a brown mass, soluble in acids with the production of a blue solution. The blue colour is destroyed by heating with lead peroxide and acetic acid, and cannot be made to reappear, whereas the homologous tetramethyldiaminodiphenylcarbinol,  $OH \cdot CH(C_6H_4 \cdot NMe_2)_2$ , when similarly treated, is first decolorised and then assumes an intense colour again on further heating. As might be expected from its constitution, the new carbinol furnishes no colouring matters when heated with aniline, dimethylaniline, or phenols in the presence of sulphuric acid. *Tetramethyldiaminodiphenylethane dihydrochloride* is a white, crystalline substance which melts and decomposes at  $225^\circ$  and is soluble in water or alcohol, but almost insoluble in acetone; the *acid sulphate*, a hygroscopic, crystalline compound, melts at  $188-189^\circ$ ; the *acetate* crystallises in long needles which redden on exposure to the air; the *phosphate*, *oxalate*, and *tartrate* have also been prepared. The base readily combines with ethyl bromide to form a *compound*,  $C_{18}H_{24}N_2 \cdot 2EtBr$ , which crystallises

in white scales melting and decomposing at  $224-225^\circ$  and is soluble in water or alcohol; the corresponding *ethiodide* derivative crystallises in large, white needles, melts and decomposes at  $228-230^\circ$ , and is soluble in water or alcohol, slightly so in acetone. Similar *compounds* are formed with methyl bromide and iodide. When treated with bromine or iodine in acetic acid solution, the base yields amorphous, unstable *compounds* of the composition  $C_{18}H_{21}Br_3N_2$  and  $C_{18}H_{21}I_3N_2$  respectively. The *dinitro*-derivative,



obtained by the action of cold nitric acid, crystallises in small, pale yellow prisms melting at  $195-196^\circ$ ; when reduced with zinc dust and acetic acid, it yields a substance which gives a splendid red coloration on oxidation. N. L.

**Naphthylated Benzidines.** By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, [ii], 60, 545-565. Compare Abstr., 1899, i, 917).—A mixture of *a*-naphthyl-*m*-phenylenediamine and dinaphthyl-*m*-phenylenediamine is obtained when equal quantities of pure *a*-naphthol and *m*-phenylenediamine are heated for some 20 hours as previously recommended for the  $\beta$ -compound. Any excess of naphthol is removed by heating the mixture to  $370^\circ$ ; the mono- and di-naphthyl compounds are best separated by the aid of boiling dilute hydrochloric acid, which dissolves out the mono-derivative in the form of its hydrochloride whereas the dinaphthyl compound remains undissolved. *a*-Naphthyl-*m*-phenylenediamine,  $C_{16}H_{14}N_2$ , distils at  $275-280^\circ$  under 15 mm. pressure, and on cooling solidifies to a yellowish-red, vitreous mass; when dissolved in benzene and precipitated by light petroleum, nodular aggregates consisting of minute, colourless needles are obtained. It melts at  $91.5-95^\circ$ , is readily soluble in hot alcohol, ether, or benzene, and to some extent in water; when kept, it turns first red and finally violet-grey. The *hydrochloride*,  $C_{16}H_{14}N_2 \cdot HCl$ , crystallises in small, colourless needles, and the *sulphate* in colourless plates.

When *m*-phenylenediamine is heated with a large excess of naphthol (4 mols.), the chief products are the mono- and di-naphthyl compounds and *a*-naphthyl oxide. *a*-Dinaphthyl-*m*-phenylenediamine,  $C_{26}H_{20}N_2$ , distils at  $345^\circ$  under 6 mm. pressure and solidifies to a pale red, vitreous mass; it crystallises from a mixture of benzene and alcohol in small, greyish needles melting at  $137.5-138^\circ$ , and is readily soluble in benzene at  $19^\circ$  (1 part in 19.3). This compound appears to exist in a second modification, as when the crude condensation product is crystallised from hot alcohol needles melting at  $101.5-102^\circ$  are obtained, which then solidify and melt a second time at  $137.5-138^\circ$ . A similar transformation occurs when the compound of low melting point is boiled with alcohol.

*a*-Naphthyl-*p*-phenylenediamine (57-67 per cent.) is formed together with the dinaphthylated base (10-12 per cent.) when the constituents are heated according to the method previously described; it crystallises from benzene and light petroleum in colourless plates, melts at  $80.5-81^\circ$ , distils at  $275-280^\circ$  under 12 mm. pressure, and is readily soluble in the ordinary organic solvents. The *hydrochloride* and *sulphate* crystallise in colourless plates. In moderately dilute acid

solution, the hydrochloride gives a dark, flocculent precipitate with ferric chloride; in extremely dilute solutions, an intense bluish-violet colour is developed. *α-Dinaphthyl-p-phenylenediamine*, obtained in larger quantities when an excess of the naphthol is employed, crystallises from hot benzene in the form of flat, colourless needles, melts at 205.5°, distils at 355° under 5 mm. pressure, and dissolves in 319 parts of benzene at 19°.

*αβ-Dinaphthyl-m-phenylenediamine* obtained from *α*-naphthyl-m-phenylenediamine and *β*-naphthol, distils at 355—358° under 6—7 mm. pressure and crystallises in needles melting at 140°. *αβ-Dinaphthyl-p-phenylenediamine* crystallises from hot benzene in glistening plates, melts at 204°, distils at 370—375° under 9 mm. pressure, and is completely decomposed when heated for 6 hours at 200° with 20 per cent. hydrochloric acid. Both compounds exhibit fluorescence in benzene solution.

J. J. S.

Wandering of the Orthoquinonoid Double Linking in Azonium Compounds. (II.) By FRIEDRICH KEHRMANN (*Ber.*, 1900, 33, 395—411. Compare Abstr., 1898, i, 439).—I. [With M. STOFFEL.]—Nitro- and Amino-flavindulines. 2-Nitroflavinduline chloride,

$$\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \equiv \text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{NPhCl} \end{array} > \text{C}_6\text{H}_3 \cdot \text{NO}_2$$
 prepared by the action of phenanthraquinone on the hydrochloride of *p*-nitro-*o*-aminodiphenylamine, separates from water in very soluble, reddish-brown needles; the *nitrate* crystallises from alcohol in transparent, reddish-brown prisms, and the *platinichloride* and *dichromate* form yellowish-red crystals. On adding sodium hydroxide, ammonia, or aniline to an alcoholic solution of the chloride, it gradually becomes clear-yellow as the base passes into the carbinol form (Abstr., 1899, i, 506; compare Hantzsch and Kalb, this vol., i, 113).

2-Amino-flavinduline hydrochloride, prepared by reducing the nitro-compound with tin and hydrochloric acid, oxidising the tin salt of the leuco-base with ferric chloride, and decomposing the tin salt of the colour-base by extracting with dilute alcohol, crystallises from water in violet-black needles, and from alcohol in short, stout, many-faced prisms; the *nitrate* is insoluble in water, but crystallises from alcohol in violet-black flakes with a metallic lustre; the *platinichloride* and the *dichromate* are blue-black or green-black, crystalline powders.

2-Acetylaminoflavinduline chloride, crystallises from alcohol in brownish-red needles with a greenish, metallic lustre; the *nitrate* is insoluble in water, but crystallises from alcohol in red prisms; the *platinichloride* and the *dichromate* are red, crystalline powders.

2:3-Diaminoflavinduline chloride, prepared by the action of ammonia on 2-aminoflavinduline chloride, is a red salt which is slightly soluble in hot water, but separates completely on cooling.

2-Amino-3-methylaminoflavinduline chloride, prepared similarly from methylamine and 2-aminoflavinduline chloride, separates from hot water in dark violet needles with a green, metallic lustre; the *nitrate* crystallises from alcohol in reddish-violet needles with a green, metallic lustre.

2-Amino-3-dimethylaminoflavinduline chloride can be obtained in long

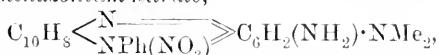
needles with a green lustre by crystallising from a mixture of alcohol and ether; the insoluble *nitrate* crystallises from alcohol in flaky crystals with a green lustre; the *platinichloride* is a violet, and the *dichromate* a green, crystalline powder.

2-Amino-3-anilino $\beta$ -fluorinduline chloride separates from dilute alcohol in large, flaky crystals; the *base* separates from dilute alcohol in reddish-brown flakes with a metallic lustre, and melts and decomposes at 290°. Phenylphenanthrophenylfluorinduline hydrochloride,

$C_{14}H_8 \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} \begin{smallmatrix} \text{=N} \\ \text{=N} \end{smallmatrix} C_6H_2 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} C_6H_5 \cdot HCl$ , prepared by fusing the preceding chloride with *o*-phenylenediamine hydrochloride and benzoic acid, crystallises from alcohol in large needles with a green lustre; on adding ammonia to an alcoholic solution of the chloride, the *base* separates in minute, golden flakes.

II. [With CH. VALENCIEN.]—Behaviour of 2-Nitro- and 2-Amino-naphthaphenazonium Salts towards Amines. By the action of ammonia on 2-nitrophenylnaphthaphenazonium chloride (Abstr., 1898, i, 155), an amino-group is introduced into the naphthalene nucleus, giving rise to 2-nitrosinduline chloride. Similarly, aniline gives a chloride and base identical with those prepared from 4-anilino- $\beta$ -naphthaquinone and nitrophenyl-*o*-phenylenediamine.

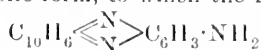
In the corresponding amino-compounds, substitution takes place in the benzene, and not in the naphthalene nucleus; this is regarded as an indication that the double bonds occupy a different position in the amino-compounds, and the latter are regarded as benzoquinone, and not naphthaquinone derivatives. 2-Amino-3-dimethylamino-5-phenylnaphthaphenazonium nitrate,



crystallises from alcohol in metallic green needles, and dissolves in water or alcohol to magenta-red solutions which become violet-blue on adding much dilute acid, owing to the formation of di-acid salts; the *dichromate* forms a dark, violet-brown, insoluble crystal powder; the *platinichloride* is a dark-brown, insoluble, crystalline powder, with a metallic lustre. 2-Amino-3-anilino $\beta$ -naphthaphenazonium-5-

*chloride*,  $C_{10}H_8 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} \begin{smallmatrix} \text{=N} \\ \text{=N} \end{smallmatrix} C_6H_2(NH_2) \cdot NHPh$ , separates from alcohol in metallic green crystals; the (anhydride-) *base* forms reddish-brown crystals with a metallic green lustre. The structure of these substances is proved by their close resemblance to the analogous compounds previously described (Abstr., 1898, i, 439; 1899, i, 238) and by the fact that they give fluorindines when fused with benzoic acid and *o*-phenylenediamine.

2-Amino-5-phenylnaphthaphenazonium chloride exists in two modifications. The stable form, to which the formula  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{=N} \\ \text{=N} \end{smallmatrix} C_6H_3 \cdot NH_2$  is assigned, dissolves in water to a dirty-violet, and in alcohol to a blue solution. The labile form, to which the formula



is assigned, is prepared by cautious reduction of the nitro-compound,

and dissolves in water or alcohol to a red-violet solution; on boiling the alcoholic solution, it passes to the stable blue form, and in a similar manner, when treated with dimethylamine gives the stable substitution product already described. The stable *acetyl* derivative, prepared from the tin salt of either modification of the chloride, crystallises from hot water in minute, red needles; the *acetylaminonitrate* is only slightly soluble, and forms minute, red, felted needles.

T. M. L.

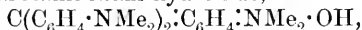
**Transformation of Colour-bases into Pseudo-ammonium Hydroxides, Cyanides, and Sulphonic Acids.** By ARTHUR HANTZSCH and G. OSSWALD (*Ber.*, 1900, 33, 278—317).—On adding one equivalent of sodium hydroxide to an aqueous solution of a diphenyl- or triphenyl-methane colour-base of the ammonium hydroxide type,  $\text{C}:\text{C} \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{CH}:\text{CH} \end{smallmatrix} \text{C}:\text{NR}'_2 \cdot \text{OH}$ , the true base is initially formed, but is rapidly converted into a colourless pseudo-base of the carbinol type,  $\text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NR}'_2$ ; the true base is soluble in water and is highly dissociated in solution, whilst the pseudo-base is insoluble and non-dissociating. The transformation of the true into the pseudo-base can therefore be studied by observing the decrease in electrical conductivity of the solution (compare *Abstr.*, 1899, i, 400, and this vol., i, 113).

In the case of the auramine base,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{OH}$ , the pseudo-base,  $\text{NH}_2 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{OH}$ , is first formed, but this immediately loses water and yields the imino-compound,



as a precipitate; the initial conductivity on liberating the base is therefore low, over 3/4 of the pseudo-base separating instantaneously in the form of the anhydride.

**Hexamethylparosanilinium hydroxide,**



liberated from "crystal violet" hydrochloride by adding one equivalent of sodium hydroxide, has  $\mu_\infty$  223.4 at 25°, and 128.2 at 0°; after being in contact with water for 5 hours at 25°, it is nearly completely converted into hexamethyltriaminotriphenylcarbinol ("crystal violet" leuco-hydroxide),  $\text{OH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$ . The conversion of the "brilliant green" base,  $\text{NEt}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NEt}_3 \cdot \text{OH}$ , into "brilliant green" leuco-hydroxide,  $\text{OH} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NEt}_3)_2$ , takes place even more rapidly. On adding sodium hydroxide to a solution of parosaniline hydrochloride, the strongly dissociating base,  $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{OH}$ , is initially formed, but after 3 hours at 25° this is completely converted into the leuco-hydroxide (triaminotriphenyl carbinol),  $\text{OH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_3$ ; it is noteworthy that the true base shows no tendency to form the imino-base,  $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ , by loss of water. Curves are given showing the rate of transformation at 0° and 25° of the true into the pseudo-bases in all the cases dealt with.

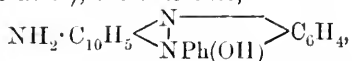
On adding sodium cyanide (1 mol.) to an aqueous solution of parosaniline hydrochloride, the true cyanide is initially formed, but after 10 minutes at 25° or 1 hour at 0°, the pseudo- or leuco-cyanide,  $\text{CN} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_3$ , begins to separate, the electrical conductivity

falling simultaneously; a curve is given showing the rate of this change. The *pseudo-cyanide*,  $\text{CN} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$  (*hexamethyltri-aminotriphenylacetone nitrile*), prepared similarly from "crystal violet," crystallises from alcohol in colourless, cruciform aggregates, and from benzene in slightly bluish needles, which, on heating, become first green, then brown, and finally melt and decompose at  $288-290^\circ$ ; the *tri-hydrochloride*,  $\text{C}_{26}\text{H}_{33}\text{N}_4\text{Cl}_3$ , forms beautiful, colourless crystals, the *mercuric chloride* derivative,  $\text{CN} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3 \cdot 3\text{HgCl}_2$ , a white powder, and the *hydriodide*, slender, colourless needles, which blacken at  $180^\circ$  and decompose at  $190^\circ$ ; with iodine, the latter yields the *periodide*,  $\text{C}_{26}\text{H}_{33}\text{N}_4\text{I}_5$ , which separates from alcohol in dark brown crystals and melts at  $183-184^\circ$ . Attempts to hydrolyse the pseudo-cyanide to the corresponding amide or carboxylic acid gave no result.

The *pseudo-cyanide*,  $\text{CN} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , derived from "malachite green," separates from a mixture of benzene and ethyl acetate in beautiful, colourless crystals, and melts and decomposes at  $176^\circ$ . "*Brilliant green*" *pseudo-cyanide*,  $\text{CN} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$ , prepared similarly, forms white crystals, melts at  $160^\circ$ , and yields a *dihydrochloride*,  $\text{C}_{25}\text{H}_{35}\text{N}_3\text{Cl}_2$ , which separates in nearly colourless crystals. It is noteworthy that none of the pseudo-cyanides described can be prepared by the interaction of hydrocyanic acid with the corresponding pseudo-bases.

"*Brilliant green*" *leucosulphonic acid*,  $\text{SO}_3\text{H} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , prepared by the action of sulphur dioxide on "*brilliant green*" leuco-hydroxide dissolved in ether, is colourless, somewhat unstable, and melts at  $154^\circ$ ; the more stable *sulphate*,  $\text{SO}_3\text{H} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2 \cdot \text{H}_2\text{SO}_4$ , prepared similarly from the sulphate of the colour base, crystallises from water in aggregates of colourless needles and melts and decomposes at  $137^\circ$ . From "crystal violet," no analogous compound can be obtained, but pararosaniline hydrochloride yields the *leucosulphonic derivative*,  $\text{SO}_3\text{H} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_3 \cdot \text{HCl} + 2\text{H}_2\text{O}$ , as a white, microcrystalline mass. Mineral acids in the cold, and aqueous alkalis on warming, remove sulphur dioxide from these sulphonic derivatives, the latter in this respect being comparable with the *syn*-diazosulphonates.

On adding sodium hydroxide to rosinduline hydrochloride ( $\mu\pi$  225.3 at  $25^\circ$ , 129.9 at  $0^\circ$ ), the true base,



initially formed, is almost instantaneously converted, by loss of water, into the insoluble pseudo-base,  $\text{NH} \cdot \text{C}_{10}\text{H}_5 \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh} \end{array} \right\rangle \text{C}_6\text{H}_4$ . With 1 mol. of sodium hydroxide, rosindone chloride,  $\text{C}_{10}\text{H}_5\text{Cl} \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPhCl} \end{array} \right\rangle \text{C}_6\text{H}_4$ , yields the stable, strongly dissociating, *true* base, chloronaphthaphenazonium hydroxide,  $\text{C}_{10}\text{H}_5\text{Cl} \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh}(\text{OH}) \end{array} \right\rangle \text{C}_6\text{H}_4$ , whilst with 2 mols., the *base*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5 \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh}(\text{OH}) \end{array} \right\rangle \text{C}_6\text{H}_4$ , appears to be formed, but gradually decomposes at  $25^\circ$ , and yields rosindone,  $\text{O} \cdot \text{C}_{10}\text{H}_5 \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh} \end{array} \right\rangle \text{C}_6\text{H}_4$ .

Flavindulinium hydroxide, liberated from the strongly dissociating chloride, is almost instantaneously converted into an insoluble pseudo-base, whilst on the other hand, the bases liberated from the hydrochlorides of phenosafranine and methylene-blue are perfectly stable in contact with water at  $0^{\circ}$ , and do not yield pseudo-forms; at  $25^{\circ}$ , water brings about secondary decomposition.

W. A. D.

**Constitution of Auramine.** By ALFRED STOCK (*Ber.*, 1900, 33, 318—320. Compare Hantzsch and Osswald, preceding abstract).—Phenylmethyllauramine hydrochloride, prepared by heating tetramethyldiaminobenzophenone hydrochloride with methylaniline, or from dimethylaminobenzomethylaniline and dimethylaniline (German Patent, 44,077), combines with ammonium thiocyanate to form a red, crystalline *thiocyanate*,  $C_{25}H_{28}N_4S$ , which, on hydrolysis with alkalis, yields methylaniline and the corresponding ketone, and with potassium cyanide gives rise to *phenylmethyllauramine hydrocyanide*,  $CN \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot NMePh$ ; this separates from ether in large, slightly yellow-coloured crystals, melts at  $99^{\circ}$ , and when warmed with alcohol gives an equilibrium with the yellowish-red, tautomeric form,  $NMe_2 \cdot C_6H_4 \cdot C(NMePh) : C_6H_4 : NMe_2 \cdot CN$ ; on adding sulphur to the solution, the latter form is converted into the thiocyanate, and a further quantity of the red hydrocyanide is then formed, which is similarly removed. From these facts, Graebe's doubts (*Abstr.*, 1899, i, 702) as to the existence of phenylmethyllauramine, and his arguments in favour of the imine formula for auramine, appear to be no longer tenable.

W. A. D.

**Synthesis of Phenylhydroxytriazoles.** By HANS RUPE and HANS LABHARDT (*Ber.*, 1900, 33, 233—246. Compare *Abstr.*, 1899, i, 356).—When the aliphatic  $\beta$ -acylphenylhydrazines are treated with carbamic chloride, the group  $CO \cdot NH_2$  is introduced into the molecule; further condensation then takes place with elimination of water, and a hydroxytriazole is produced.

*1-Phenyl-3-methyl-5-ketotriazole-4-carbamide*,  $NH_2 \cdot CO \cdot N \begin{smallmatrix} CMe:N \\ CO-NPh \end{smallmatrix}$ , prepared by mixing carbamic chloride with  $\beta$ -acetylphenylhydrazine suspended in dry benzene, crystallises from alcohol in colourless needles melting at  $154$ — $155^{\circ}$ . A small quantity of phenylmethyl-oxydiazole (*Abstr.*, 1890, 1440) may be isolated from the benzene mother liquors; this compound is produced by the interaction of between  $\beta$ -acetylphenylhydrazine and the carbonyl chloride present in the carbamic chloride. The action of carbonyl chloride on other  $\beta$ -acylphenylhydrazines in boiling benzene gives rise to homologous diazoles.

*1-Phenyl-3-benzoyloxydiazolone*, obtained from  $\alpha$ -acetyl- $\alpha\beta$ -diphenylhydrazine, crystallises in leaflets melting at  $68^{\circ}$ ; it is readily hydrolysed by acids or alkalis.

*5-Hydroxy-1-phenyl-3-methyltriazole*, produced by hydrolysing the preceding carbamide, crystallises in leaflets melting at  $163$ — $164^{\circ}$ , and is identical with the compound obtained by Andreocci (*Abstr.*, 1890, 889), from acetylurethane and phenylhydrazine.



1-Phenyl-5-ketotriazole-4-carbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \begin{smallmatrix} \text{CH:N} \\ \text{CO-NPh} \end{smallmatrix}$ , obtained by the action of carbamic chloride on  $\beta$ -formylphenylhydrazine, melts at  $163\text{--}164^\circ$ ; it is readily hydrolysed into 5-hydroxy-1-phenyltriazole,  $\text{CH} \begin{smallmatrix} \text{N:NPh} \\ \text{N:C}\cdot\text{OH} \end{smallmatrix}$ , which crystallises in colourless leaflets or prisms, melts at  $179\text{--}181^\circ$ , and resembles its methyl homologue in its solubility in organic solvents and in solutions of the alkalis.

5-Acetoxy-1-phenyltriazole, produced by the action of acetic anhydride and anhydrous sodium acetate on the preceding compound, crystallises in colourless needles; the acetyl group is readily removed with the formation of the original triazole.

1-Phenyl-3-ethyl-5-ketotriazole-4-carbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \begin{smallmatrix} \text{CEt:N} \\ \text{CO-NPh} \end{smallmatrix}$ , from carbamic chloride and  $\beta$ -propionylphenylhydrazine, melts at  $148^\circ$ , and resembles its lower homologues.

5-Hydroxy-1-phenyl-3-ethyltriazole,  $\text{CEt} \begin{smallmatrix} \text{N:C}\cdot\text{OH} \\ \text{N:NPh} \end{smallmatrix}$ , produced from the preceding compound by alkaline hydrolysis, crystallises in white needles, and resembles its homologues; the *acetoxy*-derivative, obtained by the action of acetic anhydride and excess of anhydrous sodium acetate, crystallises in radiate aggregates of colourless needles and melts at  $62\text{--}63^\circ$ .

1-Phenyl-4-methyl-3-ethyl-5-ketotriazole,  $\text{NMe} \begin{smallmatrix} \text{CEt:N} \\ \text{CO-NPh} \end{smallmatrix}$ , prepared by heating 5-hydroxy-1-phenyl-3-ethyltriazole with sodium methoxide and methyl iodide in methyl alcohol solution at  $100^\circ$ , crystallises from dilute alcohol in prisms melting at  $77\text{--}78^\circ$ ; it is insoluble in alkalis and not affected by hydrochloric acid.

Carbamic chloride has no action on  $\beta$ -benzoylphenylhydrazine, but the carbonyl chloride present in the impure reagent gives rise to diphenyloxydiazolone.

5-Hydroxy-1-phenyl-3-benzyltriazole,  $\text{CH}_2\text{Ph} \cdot \text{C} \begin{smallmatrix} \text{N:NPh} \\ \text{N:C}\cdot\text{OH} \end{smallmatrix}$ , obtained by the action of carbamic chloride on  $\alpha$ -acetyl- $\alpha\beta$ -diphenylhydrazine, crystallises from alcohol in lustrous, colourless leaflets and melts at  $187^\circ$ ; the intermediate carbamide could not be isolated in this case. The triazole is very stable towards acids and alkalis.

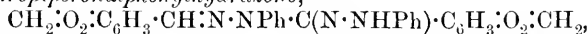
When carbamic chloride interacts with phenylsemicarbazide, 3:5-dihydroxy-1-phenyltriazole is produced (Pinner, *Abstr.*, 1888, 687).

G. T. M.

Dipiperonaldiphenylhydrotetrazone and its Isomeric Transformations. By GAETANO MINUNNI (*Gazzetta*, 1899, 29, ii, 420—434). —Dipiperonaldiphenylhydrotetrazone,  $\text{N}_2\text{Ph}_2(\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}_2\cdot\text{CH}_2)_2$ , prepared by oxidising piperonalphenylhydrazone in ethereal solution by means either of amyl nitrite or mercuric oxide, separates from benzene in small, yellow prisms or leaflets, soluble in acetone or chloroform. It dissolves readily in concentrated sulphuric acid, forming a

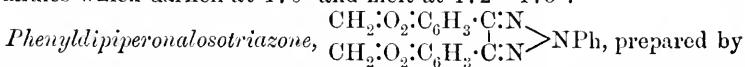
violet coloration which rapidly turns brown. When heated slowly, it softens at  $147^{\circ}$  and melts at  $148-149^{\circ}$  or at  $150-152^{\circ}$ , but with quicker heating turns brown at  $155^{\circ}$  and melts at  $156-157^{\circ}$ . The limpid, fused mass does not crystallise on cooling. Benzoyl chloride or alcoholic potash converts it into piperil- $\beta$ -osazone, prepared by Biltz and Wienands (Abstr., 1899, i, 911); when heated with an excess of benzoyl chloride, piperil- $\beta$ -osazone gives rise to a small quantity of a compound which separates from benzene by the addition of alcohol in almost white flocks melting at above  $240^{\circ}$ .

*Dehydropiperonalphenylhydrazone*,



obtained by the action of heat on dipiperonalaldiphenylhydrotetrazone, separates from benzene on the addition of alcohol in reddish-brown granules which darken at  $170^{\circ}$  and melt at  $172-173^{\circ}$ .

*Phenylpiperonalosotriazone*,

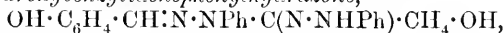


the dry distillation of piperil- $\beta$ -osazone, separates from dilute alcohol in white, microscopic crystals melting at  $153-155^{\circ}$ . T. H. P.

**Oxidation of Cinnamaldehydephenylhydrazone.** By GAETANO MINUNNI and GIOVANNI ORTOLEVA (*Gazzetta*, 1899, 29, ii, 434-436).—By oxidising cinnamaldehydephenylhydrazone in chloroform solution by means of mercuric oxide, *dehydrocinnamaldehydephenylhydrazone* (?),  $\text{CHPh}:\text{CH}:\text{CH}:\text{N}\cdot\text{NPh}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}:\text{CHPh}$ , is obtained in small quantity; it separates from benzene on the addition of alcohol in minute, yellow crystals which soften at  $200^{\circ}$  and melt at  $203-204^{\circ}$ .

T. H. P.

**Oxidation of Salicylaldehydephenylhydrazone.** By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 437-443).—On oxidising salicylaldehydephenylhydrazone by means of amyl nitrite, *dehydro-o-hydroxybenzylidenephylhydrazone*,

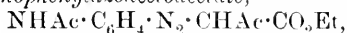


is obtained; it is soluble in benzene, from which it is deposited, on adding alcohol, in yellowish flocks of minute, acicular crystals which melt and evolve gas at  $210^{\circ}$ . Sulphuric acid dissolves it with the formation of a greenish solution. Its *tribenzoyl* derivative,  $\text{C}_{26}\text{H}_{19}\text{O}_2\text{N}_4\text{Bz}_3$ , separates from its benzene solution on the addition of alcohol either slowly in the form of large, yellowish, prismatic crystals, or quickly as slender needles melting at  $156-157^{\circ}$  to a black liquid. T. H. P.

**Benzylidene Derivatives of Triaminodiphenylamine.** By MAX GRONEBERG (*Ber.*, 1900, 33, 215-218).—4:2':4'-*Tribenzylidenetriaminodiphenylamine*,  $\text{CHPh}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{N}:\text{CHPh})_2$ , is obtained by the action of benzaldehyde on 4:2':4'-triaminodiphenylamine and decomposes when heated. When treated with dilute acids, benzaldehyde is regenerated to some extent, and a light grey, amorphous substance obtained which melts at  $122-124^{\circ}$  to a brown syrup, and has the composition of a *sesquibenzylidenetriaminodiphenylamine*,  $\text{CHPh}[\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NH}_2):\text{N}:\text{CHPh}]_2$ . The *ovalate* is a light green, bulky powder.

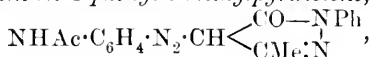
A. H.

Aliphatic-aromatic Azo- and Tetrazo-derivatives of *p*-Phenylenediamine. By CARL BÜLOW (*Ber.*, 1900, 33, 187—199).—*Ethyl-α-p-acetaminophenylazoacetate*,



prepared by combining *p*-acetaminodiazobenzene chloride with ethyl acetoacetate, crystallises from dilute alcohol in stout, yellow needles, melts at 148°, and on warming with aqueous ammonia yields the corresponding *amide*,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_3 \cdot \text{CO} \cdot \text{NH}_2$ , which forms yellow, lustrous needles, and melts and decomposes at 228—229°; methylamine gives rise to the *methylamide*,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_3 \cdot \text{CO} \cdot \text{NHMe}$ , which crystallises from alcohol or glacial acetic acid in sulphur-yellow needles.

*4-p-Acetaminobenzeneazo-1-phenyl-3-methylpyrazolone*,



prepared by adding phenylhydrazine acetate to a boiling alcoholic solution of ethyl *α-p*-acetaminophenylazoacetate, crystallises from alcohol in slender, yellowish-red, felted needles and melts at 222—223°; on hydrolysis with either boiling aqueous sodium hydroxide or 10 per cent. alcoholic hydrochloric acid, it yields the corresponding *base*, which crystallises from alcohol in brownish-red, highly lustrous prisms, melts at 206—207°, and yields a *benzoyl* derivative crystallising in lustrous, orange-yellow leaflets and melting at 238°. On combining the diazo-chloride of the base with ethyl acetoacetate, the *tetrazo*-compound

$\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} \begin{array}{l} \text{CO—NPh} \\ \text{CMe:N} \end{array}$ , is obtained; this separates

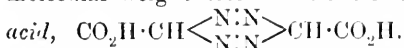
from alcohol in vermilion crystals, melts at 181—182°, and, with phenylhydrazine, yields *p-bis-1-phenyl-3-methylpyrazoloneazobenzene*,  $\text{C}_6\text{H}_4 \left( \text{N:N} \cdot \text{CH} \begin{array}{l} \text{CO—NPh} \\ \text{CMe:N} \end{array} \right)_2$ , which crystallises in red needles and does not melt at 280°.

All the compounds described possess feebly acid properties, dissolving unchanged in warm dilute aqueous alkalis to yield coloured solutions; this behaviour is probably due to the  $\cdot\text{CH}$  group contiguous to the carbonyl radicle.

W. A. D.

**Polymerisation Products from Ethyl Diazoacetate.** By ARTHUR HANTZSCH and OSWALD SILBERRAD (*Ber.*, 1900, 33, 58—89. Compare Curtius and Lang, *Abstr.*, 1889, 369).—Several improvements in the preparation of ethyl aminoacetate hydrochloride are recommended. One is the careful granulating, while hot, of the mixture of glycocine hydrochloride and ammonium chloride and the subsequent drying of this in a large Victor Meyer bath at 115°.

The compound obtained by Curtius and Lang from ethyl diazoacetate and described as tridiazooacetic acid is shown, by the aid of molecular weight determinations of the ethyl ester, to be *bisdiazooacetic acid*,

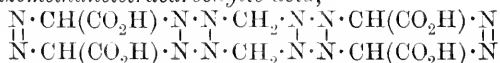


In its preparation, the impure sodium bisdiazooacetate is first washed with alcohol, then rubbed into a paste with water, and again treated in a similar manner until all carbonate is removed; if not thus purified,

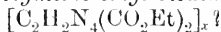
much hydrazine is formed on subsequent treatment with sulphuric acid. A 25 per cent. yield of the ethyl ester is obtained when the precipitated silver salt is washed with alcohol, ether, benzene, and then warmed with a benzene solution of slightly less than the theoretical amount of ethyl iodide; it melts at  $113.5^\circ$  and not at  $110^\circ$ . The silver salt exhibits characteristic colours with nitric acid which may be made use of in testing even impure bisdiazooacetic acid. The hydrates represented by Curtius and Lang as  $C_3H_3N_6(CO_2H)_3 \cdot 3H_2O$  and  $2H_2O$  are to be represented as  $C_3H_2N_4(CO_2H)_2 \cdot 2H_2O$  and  $H_2O$  respectively. The statement that the hydrated salt, when heated at  $100^\circ$ , is easily converted into carbon dioxide and tetrazine cannot be substantiated. The anhydrous acid is obtained together with dihydrotetrazine when the hydrated acid is boiled with absolute alcohol; it forms a pale yellow powder melting at  $180^\circ$ , and is insoluble in ordinary solvents, but dissolves readily in alkalis; at  $100^\circ$ , it is slowly, but at its melting point rapidly, converted into carbon dioxide and dihydrotetrazine.

*Dihydrotetrazinedicarboxylic acid*,  $CO_2H \cdot C \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{N} \cdot \text{NH} \end{smallmatrix} \cdot C \cdot CO_2H$ , is formed when bisdiazooacetic acid is treated with potassium hydroxide, or as a by-product in the conversion of ethyl diazoacetate into trisbisdiazomethanetetra-carboxylic acid; it forms long, colourless, glistening needles melting and decomposing at  $287^\circ$ , is sparingly soluble in water and even more sparingly in other solvents; the *potassium* salt crystallises in thick, colourless prisms and the *silver* salt forms a gelatinous precipitate.

*Trisbisdiazomethanetetra-carboxylic acid*,

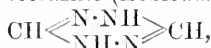


(Curtius and Lang's dicarboxylic acid), is obtained, together with the acid just described, by the action of potassium hydroxide on ethyl diazoacetate, but the separation is tedious; it forms long, colourless, hair-like needles which melt at  $183^\circ$ , and yield diazomethane. The *silver* salt,  $3C_6H_8N_{12}(CO_2Ag)_4 \cdot 4AgNO_3$ , forms a white powder, which, on treatment with ethyl iodide, yields a considerable amount of tarry matter together with a *polymeric ethyl bisdiazooacetate*,



which crystallises from alcohol in glistening plates melting at  $232^\circ$ . The compound obtained by Curtius and Lang on heating the acid, and stated to be  $C_3H_6N_6$ , is shown to have the formula  $C_2H_4N_4$  and is 3:6-dihydro-1:2:4:5-tetrazine (bisdiazomethane),  $CH_2 \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{N} \cdot \text{N} \end{smallmatrix} CH_2$ ; its melting point, after recrystallisation from alcohol, is  $149^\circ$ , and after sublimation  $154^\circ$ ; Curtius and Lang gave  $145^\circ$ .

1:4-Dihydro-1:2:4:5-tetrazine (isobisdiazomethane),



Curtius and Lang's trimethintriazimide, may be obtained by the following methods: 1. By allowing bisdiazomethane to remain in contact with alcoholic potash for several weeks. 2. By heating dihydrotetrazinedicarboxylic acid with dilute hydrochloric acid. 3. By

heating bisdiazooacetic acid at its melting point. 4. By heating formylhydrazine at  $156^{\circ}$  (Ruhemann and Stapleton, *Trans.*, 1899, **75**, 1131). It is, however, most readily obtained by heating crude bisdiazooacetic acid with absolute alcohol and a small amount of ethyl cinnamate; if the substances employed are not dry, a considerable amount of hydrazine formate is produced.

Dihydropyrazine hydrochloride,  $C_2H_4N_4 \cdot HCl$ , melting at  $151^{\circ}$  (compare Pellizzari, *Abstr.*, 1899, **i**, 859), platinichloride (Ruhemann and Stapleton, *loc. cit.*), *hydrobromide*, melting and decomposing at  $136^{\circ}$ , *hydriodide*, melting and decomposing at  $134$ — $135^{\circ}$ , *oxalate*,  $C_2H_4N_4 \cdot H_2C_2O_4$ , microscopic needles melting and decomposing at  $164^{\circ}$ , and an *acetyl* derivative,  $CH \begin{smallmatrix} \swarrow N \cdot Ac \\ \searrow N \cdot NH \end{smallmatrix} CH$ , a syrup which slowly crystallises, have been prepared.

Sodium amalgam has no action on dihydropyrazine; with tin and hydrochloric acid, it yields ammonium salts; with zinc dust and acetic acid, a small amount of methylhydrazine is obtained. When treated with benzoyl chloride by the Schotten-Baumann method, it is converted into *s*-dibenzoylhydrazine melting at  $238^{\circ}$ ; Curtius (*Abstr.*, 1891, **i**, 56) and Struve (*ibid.*, 1895, **i**, 35) give  $233^{\circ}$ , and Borrisow (*Zeit. physiol. Chem.*, 1894, **19**, 505)  $237^{\circ}$ .

Most oxidising agents either do not attack dihydropyrazine or else completely destroy it; when, however, nitrous anhydride is led into an aqueous solution of the tetrazine at  $0^{\circ}$ , and, after some time, the solution evaporated, colourless crystals of 1:2:4-*triazole nitrate*,

$NH \begin{smallmatrix} \swarrow CH \cdot N \\ \searrow CH \cdot N \end{smallmatrix} HNO_3$ , are formed; this separates from alcohol in octa-

hedral twinned crystals or in needles melting at  $138^{\circ}$ , and sublimes when carefully heated; it yields the following double salts:

$3(C_2H_3N_3 \cdot HNO_3) \cdot 4AgNO_3$ , white precipitate;  $C_2H_3N_3 \cdot HNO_3 \cdot 2HgCl_2$ , large, octahedral-shaped crystals;  $C_2H_3N_3 \cdot NaNO_3$ , small, colourless needles;  $C_2H_3N_3 \cdot AgNO_3$  or  $C_2H_2AgN_3 \cdot HNO_3$ , heavy precipitate;  $C_2H_2(CuNO_3)N_3$ , blue precipitate.

Free triazole cannot be obtained by the action of alkalis on the nitrate; it is best formed by treating the hydrochloride with silver oxide. The product thus formed is identical with that obtained by Freund and Meineke (*Abstr.*, 1897, **i**, 113). The *hydrochloride* is obtained when the nitrate is heated with concentrated hydrochloric acid at  $150^{\circ}$ , or better, by reducing the nitrate with sodium amalgam and alcohol, and then treating with alcoholic hydrogen chloride. It forms colourless, rhombic plates melting at  $168$ — $169^{\circ}$ , and is readily soluble in water. J. J. S.

**Diazocaffeine.** By MOSES GOMBERG (*Amer. Chem. J.*, 1900, **23**, 51—69).—When aminocaffeine, dissolved in strong hydrochloric acid, is treated with a solution of sodium nitrite at  $-10^{\circ}$ , a solution is obtained which exhibits all the reactions of a diazo-compound; it stains the skin a dark red, quickly changing to brown, and on raising the temperature of the liquid, a gas, probably nitrogen, is evolved, and a small quantity of a very bulky, amorphous compound separates

Diazocaffeine also appears to be produced by the action of nitric acid on aminocaffeine in the cold.

*Caffeine-p-azophenol*,  $C_8H_9O_2N_4 \cdot N_2 \cdot C_6H_4 \cdot OH$ , formed on mixing solutions of diazocaffeine hydrochloride and phenol, crystallises from acetic acid in red needles insoluble in cold water.

*Caffeine-p-azodimethylaniline*,  $C_8H_9O_2N_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2$ , separates from boiling chloroform on addition of ether in long, dark red needles, having a beautiful, greenish iridescence, and on pouring the hot solution in chloroform into boiling toluene is precipitated in the form of dark, steel-blue needles. It is scarcely soluble in water, sparingly soluble in alcohol, benzene, or dilute acetic acid. The *hydrochloride* is fairly stable when dry, but easily decomposed by water. On reduction with stannous chloride, the substance yields dimethylaniline and aminocaffeine.

*Caffeine-azo-2:4-diaminobenzene*,  $C_8H_9O_2N_4 \cdot N_2 \cdot C_6H_3(NH_2)_2$ , is brown, dissolves sparingly in the usual media, and does not melt at  $285^\circ$ .

*Caffeine-azo- $\beta$ -naphthol*,  $C_8H_9O_2N_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$ , separates from glacial acetic acid in minute, ponceau-red needles, and is soluble in hot benzene and chloroform.

When diazocaffeine is allowed to react with acetoacetic acid, an *azo-compound*,  $COMe \cdot C(N_2 \cdot C_8H_9O_2N_4)_2 \cdot CO_2H$ , is produced, which crystallises in dark blue crystals with a green reflex, and is sparingly soluble in alcohol or benzene, but fairly soluble in water or chloroform. It shows signs of fusion at  $200^\circ$ , but is not melted at  $285^\circ$ .

With propylacetoacetic acid, diazocaffeine affords a dark brown, crystalline *substance*,  $CPr^a(N_2 \cdot C_8H_9O_2N_4)_2 \cdot CO_2H$ , which has a bluish tint, but no metallic lustre, and is sparingly soluble in water; it does not melt at  $285^\circ$ .

The *compound*,  $C_7H_7 \cdot C(N_2 \cdot C_8H_9O_2N_4)_2 \cdot CO_2H$ , obtained with benzylacetoacetic acid, forms dull black crystals from a mixture of chloroform and ether, and does not melt at  $285^\circ$ .

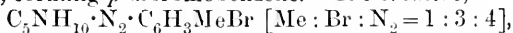
Diazocaffeine acts on an alkaline solution of nitroethane, forming a *substance*,  $NO_2 \cdot CMe(N_2 \cdot C_8H_9O_2N_4)_2$ , which separates from a mixture of chloroform and ether in deep blue flakes melting at  $218-219^\circ$ .

With nitropropane and diazocaffeine, a similar *compound* is obtained, which forms very light, deep blue flakes, having a slight metallic lustre and melting with decomposition at  $237-238^\circ$ . A. L.

**Mixed Diazoamino-compounds.** By OTTO WALLACH and A. TEWES (*Chem. Centr.*, 1899, ii, 1050-1051; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—The *compound*,

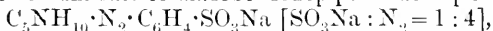
$C_5NH_{10} \cdot N_2 \cdot C_6H_4 \cdot CO_2H$  [ $CO_2H : N_2 = 1 : 2$ ], prepared by the action of piperidine on diazotised *o*-aminobenzoic acid, crystallises in white leaflets, melts at  $84^\circ$ , and forms an ammonium salt which is insoluble in ether, and a silver salt which crystallises in colourless needles. The isomeric *meta*-compound, prepared similarly from diazotised *m*-aminobenzoic acid, melts at  $123^\circ$  and the *para*-compound melts and decomposes at  $158^\circ$ . By the action of diazotised *p*-aminophenol on piperidine, the *compound*,  $C_5NH_{10} \cdot N_2 \cdot C_6H_4 \cdot OH$  [ $OH : N_2 = 1 : 4$ ], is formed; it melts at  $87-88^\circ$ . The corresponding *com-*

*pound*,  $C_5NH_{10} \cdot N_2 \cdot C_6H_4 \cdot OMe$ , similarly prepared from anisidine, crystallises in large, yellow crystals, and melts at  $33-34^\circ$ . The reactions of the preceding compounds resemble those of benzene-diazopiperidide. By the action of bromine, dissolved in carbon disulphide, on benzene-diazopiperidide, the *hydrobromide*,  $C_5NH_{10} \cdot N_2Ph \cdot HBr$ , is precipitated, whilst the *bromide*,  $C_5NH_{10} \cdot N_2 \cdot C_6H_4Br$  [ $Br : N_2 = 1 : 4$ ], remains in solution. The former compound, when warmed with dilute sulphuric acid, yields phenol, together with a considerable amount of tribromophenol, which melts at  $92^\circ$ . The bromide crystallises in yellow leaflets, melts at  $55^\circ$ , and is decomposed by warming with concentrated hydrobromic acid, forming *p*-dibromobenzene. The *bromide*,



obtained by the action of bromine on *p*-toluenediazopiperidide, forms yellow crystals, melts at  $52-53^\circ$ , and when boiled with concentrated hydrobromic acid yields 3:4-dibromotoluene.

When the sodium salt of diazobenzenepiperididesulphonic acid,



is treated with bromine in the cold, dibromodiazobenzeneperbromide,  $C_6H_3Br_2 \cdot NBr \cdot NBr_2 [N_2 : Br_2 = 1 : 3 : 4]$ , is formed. When the perbromide is boiled with alcohol, it yields 1:2:4-tribromobenzene, and by the action of ammonia it forms diazobenzeneimide. The imide melts at  $62^\circ$ , is volatile in steam, and when boiled with concentrated hydrobromic acid forms 2:4:6-tribromoaniline.

In the conversion of diazobenzenepiperididesulphonic acid into dibromodiazobenzene perbromide, the replacement of the sulphonic group by bromine in ice-cold solutions is remarkable. E. W. W.

**Nitrogen which can be split off from Proteids by Acids.** By YANDELL HENDERSON (*Zeit. physiol. Chem.*, 1900, 29, 47—50).—Hausmann has stated (*Abstr.*, 1899, i, 653) that the amount of nitrogen obtainable in various forms by decomposing proteid with acids is characteristic for different proteids. This is not so; with either hydrochloric or sulphuric acid, the amount of nitrogen is most variable, depending on the concentration of the acid and the duration of the action. W. D. H.

**Nitrogen in Primary Albumoses.** By ERNST FRIEDMANN (*Zeit. physiol. Chem.*, 1900, 29, 51—58).—The nitrogen obtained from primary albumoses (proto- and hetero-albumose) was estimated as loosely bound nitrogen, basic nitrogen, and acid nitrogen by Hausmann's method. The two proteids gave different results. The results are different from those previously given by Pick and by Hausmann, and if the criticism of the method contained in the preceding abstract is upheld, this is easily accounted for. W. D. H.

**Physical alterations in Proteids.** By W. PAULI (*Pflüger's Archiv*, 1899, 78, 315—345).—The investigation was undertaken with the view of elucidating the colloidal condition of proteids, the special point selected being the coagulation temperature and its variations when different amounts of various neutral salts are added to the solution. Thus a gradual increase in the percentage of various chlorides raises the coagulation temperature up to a certain point, when it begins to fall again; this is most marked with the chlorides

of lithium, magnesium, and barium; the alteration of the coagulating point is not absolutely proportional to the amount of salt added. Similar results were obtained with the bromides; iodides, on the other hand, depress the coagulation temperature. Various other groups of salts, nitrates, sulphates, acetates, &c., were also investigated, and the results of different salts of the same metal compared. The influence of pairs of salts on coagulation temperature was also examined. The results, as well as the effect of precipitation of globulin by neutral salts, are believed to be due to the entrance of ions into the proteid molecule.  
W. D. H.

**Oxidation of Crystalline Egg-albumin by Hydrogen Peroxide.** By FRIEDRICH W. SCHULZ (*Zeit. physiol. Chem.*, 1900, 29, 86—104).—By the action of hydrogen peroxide on crystallised egg-albumin, a new substance, *oxyprotein*, with the general characters of oxyprotosulphonic acid, is obtained; this is an oxidation product, not a decomposition product of albumin. There is, however, a difference between the two substances mentioned; the sulphur of the proteid which can be removed by alkali is not oxidised, but is so much diminished that more delicate methods have to be adopted for its detection. The hydrolysing action of hydrogen peroxide is ascribed to the fact that this reagent strengthens the hydrolysing action of acid and alkalis. The crystalline proteid used in these experiments was prepared by the acid method; it differs from the crystalline egg-albumin prepared by Hofmeister's method in elementary composition, and is probably in a hydrated condition.  
W. D. H.

**Crystallised Fibrin.** By LOUIS MAILLARD (*Compt. rend.*, 1900, 130, 192—194. Compare Abstr., 1899, i, 466, and ii, 777).—Prolonged treatment of the granular deposit from antidiphtheric serum with boiling alcohol and 5 per cent. hydrochloric acid destroys the crystallised fibrin, but even after 6 hours digestion with the acid, small granules of a crystalline substance remain. An examination of the product by the aid of the polarising microscope and micro-chemical reactions indicates the presence of a proteid substance in different stages of crystallogenesis; some of the granules obtained from serum after four years exhibit a distinctly crystalline character when viewed in polarised light. The deposit, before treatment with hydrochloric acid, also contains spherical aggregates of doubly refracting needles, having the properties of calcium palmitate.  
G. T. M.

**The Proteids of Cows' Milk.** By KARL STORCH (*Monatsh.*, 1899, 20, 837—846).—Full directions are now given for the purification of the substances *a* and *b* previously described (compare Abstr., 1897, ii, 420). Substance *a* is a nucleo-albumin, characterised by its composition, acid reaction, insolubility in water and concentrated solutions of sodium sulphate, magnesium sulphate, or sodium chloride, also by its solubility in small quantities of alkali, sodium carbonate, or lime-water, to solutions of neutral reaction, and by remaining uncoagulated when such solutions are boiled.



Substance *b* is a nucleo-histon, and is characterised by its composition and behaviour towards water, acids, alkalis, and neutral salts, especially by the fact that 0·8 per cent. hydrochloric acid decomposes it into a soluble and an insoluble portion; the former may be precipitated by alcohol or ammonia in excess, and has the properties of a histon; the latter has those of a nuclein. Other properties of *a* and *b* are minutely tabulated. The average percentage composition is as follows, Hammarsten's analysis of casein being added for comparison:

	C.	H.	N.	S.	P.	O.
Substance <i>a</i> .....	54·43	6·805	14·815	0·635	0·79	22·525
Substance <i>b</i> .....	49·125	5·91	14·13	1·585	2·085	27·135
Casein (Hammarsten)	53·0	7·0	15·7	0·8	0·85	22·65

R. L. J.

**Formation of Methæmoglobin.** By GUSTAV HÜFNER (*Chem., Centr.*, 1899, ii, 484; from *Arch. Anat. Phys.*, 1899, 491—499. Compare von Zeynek, this vol., i, 196).—Hoppe-Seyler's theory of the formation of methæmoglobin from oxyhæmoglobin by elimination of only a portion of the oxygen is not correct, for in the action of potassium ferricyanide on oxyhæmoglobin, not one but two atoms of oxygen are set free. Hydroxylamine hydrochloride also causes a rapid conversion of oxyhæmoglobin into methæmoglobin, but hydrazine hydrate only reduces oxyhæmoglobin to hæmoglobin, which is then decomposed by excess of the hydrate forming hæmochromogen. Since albumin and the colouring matter containing iron are formed by the reducing action of hydrazine hydrate, probably both these atomic complexes are contained in hæmoglobin, and are combined in the molecule by means of oxygen.

E. W. W.

**Nucleic Acid from Salmon Milt.** By OSWALD SCHMIEDEBERG (*Chem. Centr.*, 1899, ii, 721—722; from *Arch. exp. Path. Pharm.*, 43, 57—83).—Pure nucleic acid was prepared from the material left by Miescher, which also contained protamine, by means of the copper-alkali method, which depends on the solubility of the copper compounds of proteid substances, and the insolubility of other copper compounds in a solution of alkali hydroxide in alcohol. From the analysis of the copper compound, the formula of nucleic acid was calculated to be  $C_{40}H_{56}O_{16}N_{14}2P_2O_5$ . By the decomposition of nucleic acid, the bases adenine and guanine are formed, and theoretically a residue of  $C_{30}H_{46}O_{15}N_42P_2O_5$ , or nucleotinphosphoric acid, should be left, but attempts to isolate this compound failed. From the solution, obtained by warming copper nucleate with adenine and guanine in dilute potassium hydroxide solution for 10—15 minutes at 40—45° and then cooling and acidifying with acetic acid, cupric chloride precipitates a substance which contains more purine bases than the original nucleic acid, but having properties very similar to this acid. Since in this case the precipitate cannot contain the bases combined in the form of esters, they are also probably combined in nucleic acid, as salts rather than as esters. The hypothetical nucleotinphosphoric acid has probably an ester-like constitution, for it is decomposed by heating with dilute hydrochloric acid, one half of the

base being more easily removed than the other, which requires a 10—20 per cent. solution of acid. Melanins containing phosphorus are formed by heating nucleic acid with hydrochloric acid.

E. W. W.

**Co-existence of a Reducing Enzyme and an Oxidising Enzyme in the Animal Organism.** By J. ABELOUS and ERNEST GÉRARD (*Compt. rend.*, 1899, 129, 1023—1025. Compare Abstr., 1899 ii, 681).—In a former communication, the authors showed that the amount of nitrite found in the liquid resulting from the action of an aqueous extract of the kidney of the horse on a nitrate decreased after the action had been going on for about 24 hours. This diminution of nitrite they now prove to be due to its oxidation by an oxidising enzyme (oxydase), which is present in the renal extract. By digesting the extract with papain or trypsin, its reducing action is almost entirely destroyed, so that the oxidising action alone goes on. Conversely, by conducting the experiment in an atmosphere of inert gas, like hydrogen, the oxidising enzyme is powerless, and the reducing enzyme alone acts.

H. R. LE S.

**Enzymes.** By N. SACHAROFF (*Chem. Centr.*, 1899, ii, 723; from *Centr. Bakt. Parasit.*, [i], 26, 189—194. Compare *ibid.*, 24, Nos. 18—19, and Abstr., 1899, ii, 786).—Photographs showing the effect of antiseptics on the power of papain of dissolving gelatin are reproduced in the original paper. From these photographs, it is evident that this power depends on the presence of a substance, iron nuclein or bionuclein, which possesses both oxidising and reducing properties. When the bionuclein is separated from the enzyme by the action of hydrogen peroxide, it loses its dissolving power, but this may be restored by adding a very small quantity of the active enzyme or of active bionuclein.

The formation of oxyglutin, the insoluble product of the action of papain on gelatin, is also shown by means of photographs. In the formation of oxyglutin, more oxygen is required than is necessary for the solution of the gelatin. The soluble gelatin is formed by the action of the enzyme as an intermediate product in the production of oxyglutin.

The gelatin dissolved in neutral solutions is to be distinguished from that which is formed in alkaline or acid liquids by the action of dilute papain solution.

E. W. W.

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## Organic Chemistry.

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**Action of Amalgamated Aluminium on Alcohols. Aluminium Alkyloxides.** By WETSCHIASLAW E. TISTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 694—770; 784—872. Compare Abstr., 1899, i, 408).—A number of aluminium alkyloxides have been prepared by the action of amalgamated aluminium on the corresponding alcohols. With absolute ethyl alcohol, the action is very slow in the cold, but quicker at 100°; the observation of Wislicenus and Kaufmann (Abstr., 1895, i, 437), that the action only occurs if traces of water are present, is hence inaccurate, as also is the statement of Konowaloff (*Pharm. Zeit. Russ.*, 1896, **35**, 328), that amalgamated aluminium does not act on alcohol containing a small quantity of water, even on boiling.

Aluminium methoxide is a light grey powder, has a sp. gr. of 1.35, and, on heating, decomposes with evolution of gases which burn with a luminous flame. The ethoxide is a grey powder melting at 134—135° and boiling at 205° under 14 mm. pressure; it has a sp. gr. 1.1423 at 20°/0° and 1.1545 at 0°/0°. Aluminium propoxide melts at 106—107°, boils at 250.5° under 16 mm. pressure, and has a sp. gr. 1.0578 at 20°/0° and 1.0650 at 0°/0°. The isobutoxide forms acicular crystals which melt at 212—214° and dissolve in benzene, ether, or isobutyl alcohol; it boils at 239° under 4 mm. pressure, and has a sp. gr. 0.9749 at 20°/0°. Aluminium *n*-butoxide crystallises in needles melting at 101.5—102°, and boiling at 284.5° under 10 mm. pressure; it has a sp. gr. 1.0251 at 20°/0°, and is soluble in the corresponding alcohol, and also in ether, benzene, or toluene. The isoamyloxide melts at 225—230°, and boils at 282° under 4 mm. pressure; it is soluble in benzene, ether, toluene, or isoamyl alcohol, and has a sp. gr. 1.0021 at 20°/0°, and 1.0117 at 0°/0°. The isopropoxide, which crystallises in octahedra of the tetragonal system, melts at 118—118.5°, boils at 136.5° under 6 mm., and at 153—155° under 15.5 mm. pressure; it has a sp. gr. 1.0346 at 20°/0°, and 1.0533 at 0°/0°. Aluminium secondary butoxide is a thick, transparent liquid boiling at 181—181.5° under 8 mm. pressure, and having a sp. gr. 0.9671 at 20°/0°; its index of refraction for sodium light at 20° is 1.44428. From methylpropylcarbinol, aluminium secondary amyloxide is obtained as a mobile liquid, solidifying to a glassy mass when cooled in a mixture of ether and solid carbon dioxide; it boils at about 210—212° under 8 mm. pressure. Trimethylcarbinol yields aluminium tertiary butoxide, which crystallises from benzene in beautiful, thick, rhombohedral plates belonging to the triclinic system: [ $a = 105^\circ$ ,  $\beta = 117^\circ$ ,  $\gamma = 100^\circ 20'$ ]; it melts at 206.5—207°, but does not distil undecomposed. Aluminium tertiary amyloxide (from dimethylethylcarbinol) melts at 199—200°, and is soluble in benzene or toluene, separating from the latter in needles or thin plates.

By measuring the quantities of hydrogen evolved in equal times during the reactions between amalgamated aluminium and various alcohols, it is found that the speed of reaction falls as the molecular weight of the alcohol increases, and that, in the case of isomeric alcohols, the speed is greater for the primary, than for the secondary, alcohol.

Amalgamated aluminium acts on ethyl acetoacetate, giving the ethyl aluminioacetoacetate obtained by Conrad by the interaction of potassium aluminate and ethyl acetoacetate (Abstr., 1878, 26). *Ethyl aluminomalonate*,  $\text{Al}[\text{CH}(\text{CO}_2\text{Et})_2]_3$ , obtained along with carbon dioxide, saturated and unsaturated hydrocarbons, ethyl acetate and alcohol, when ethyl malonate and amalgamated aluminium interact, crystallises from benzene in long, lustrous needles melting at  $94-95^\circ$ .

The aluminium derivatives of isobutyl and isoamyl alcohols, and of ethyl acetoacetate and malonate, have molecular weights in freezing benzene corresponding with those required for the formula  $\text{Al}(\text{OR})_3$ .

The differences between the boiling points (at the same pressure) of two consecutive members of the homologous series of aluminium alkyloxides vary from  $41^\circ$  to  $43^\circ$ , and the secondary alcohol derivatives have boiling points approximately  $100^\circ$  lower than those of the isomeric primary compounds.

Water acts on the aluminium alkyloxides, converting them into aluminium hydroxide and the corresponding alcohol. On warming aluminium alkyloxides derived from primary alcohols with other primary alcohols, replacement of the alkyl radicle with the higher molecular weight takes place more easily than the inverse reaction; and, if the alcohols are isomeric, the primary replaces the secondary, and the latter replace the tertiary from combination with aluminium. This reaction may be used in the preparation of aluminium alkyloxides not otherwise obtainable; for example, *aluminium allyloxide*,  $\text{Al}(\text{OC}_3\text{H}_5)_3$ , is obtained by the interaction of allyl alcohol and the aluminium derivative of dimethylethylcarbinol in benzene solution; it is a white powder which melts and decomposes at about  $150^\circ$ , and dissolves slightly in allyl alcohol or benzene. It has a sp. gr. 1.1861 at  $20^\circ/0^\circ$ . This compound is the first aluminium derivative of an unsaturated alcohol which has been prepared.

Hydrochloric acid acts on aluminium isopropoxide or isobutoxide, yielding a compound of the corresponding alcohol with aluminium chloride— $\text{AlCl}_3 \cdot 3\text{C}_3\text{H}_7 \cdot \text{OH}$  or  $\text{AlCl}_3 \cdot 3\text{C}_4\text{H}_9 \cdot \text{OH}$ ; these compounds are hygroscopic and are decomposed by water. On ethyl or isopropyl iodide, ethylene bromide, or chloroform, the aluminium alkoxides have no action.

[With A. GABOUNIA.]—On heating aluminium isopropoxide with  $\beta\gamma$ -dibromopropyl alcohol, *aluminium  $\beta\gamma$ -dibromopropoxide*,  $(\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{O})_3\text{Al}$ , is obtained as a colourless, porous mass, which, on keeping, assumes a reddish tint.

[With M. G. KISSELEFF.]—Acetic anhydride acts on aluminium ethoxide, giving ethyl acetate and aluminium acetate. The latter, hitherto only known in solution, is a light, white powder smelling of acetic acid, owing to decomposition by the moisture of the air. It

dissolves in cold water, and the solution may be boiled without decomposing. With aluminium ethoxide, carbon dioxide forms aluminium diethoxyethylcarbonate,  $\text{Al}(\text{OEt})_2 \cdot \text{CO}_2\text{Et}$ . Sulphur dioxide yields an analogous compound of the composition  $\text{OEt} \cdot \text{Al}(\text{SO}_2\text{Et})_2$ .

When subjected to dry distillation, the aluminium alkyl oxides, as a rule, decompose, yielding the corresponding ether, alcohol, and ethylene hydrocarbon, small quantities of aldehydes, hydrogen, and paraffinoid hydrocarbons being also obtained.

[With N. N. PUSHIN.]—Aluminium methoxide, when heated, is first resolved into alumina and dimethyl ether, the latter partially decomposing at higher temperatures with the formation of methane, carbon monoxide, and hydrogen in about equal volumes. In the case of the aluminium derivative of trimethylcarbinol, the pure alcohol is obtained without any admixture of the corresponding ether. These results are, on the whole, concordant with those obtained by Gladstone and Tribe (*Trans.*, 1882, 41, 5).

Dimethyl ether, when heated, splits up first into methane and formaldehyde, the latter at higher temperatures being resolved into equal volumes of hydrogen and carbonic oxide.

[With N. MARAZOUEFF.]—Methyl ethyl and methyl propyl ethers, when heated, suffer decomposition, with formation of carbon monoxide, hydrogen, and hydrocarbons of the ethylene series. Other ethers give similar results.

T. H. P.

**Rancidity of Fats.** By ISKAR NAGEL (*Amer. Chem. J.*, 1900, 23, 173—176).—In refining rancid fats or oils, the free fatty and unsaturated acids are removed as sodium salts by means of an aqueous solution of sodium silicate; the non-volatile lactones are removed, after this treatment, by converting them into salts of hydroxy-fatty acids by boiling for several hours with a small quantity of aqueous sodium carbonate or hydroxide. Non-volatile aldehydes are eliminated by warming with aqueous sodium hydrogen sulphite, whilst the non-volatile acetals are removed by heating the oil with dilute sulphuric acid. Alcohols, esters of fatty and hydroxy-acids, volatile aldehydes, acetals, and terpenes are removed finally by steam distillation.

W. A. D.

**Japan Wax.** By ADOLF C. GEITEL and G. VAN DER WANT (*J. pr. Chem.*, 1900, [ii], 61, 151—156. Compare Eberhardt, *Inaug. Diss.*, Strassburg, 1888).—Two samples of the wax gave, on hydrolysis, soluble acids, 5.96 and 4.66; insoluble acids, 90.62 and 90.66; total acids, 96.58 and 95.92 respectively. The soluble acids were of fatty consistency, only soluble in a large bulk of water, and gave soluble alkali-salts, but sparingly soluble barium and calcium salts; the green copper salt, on analysis, gave numbers corresponding with the formula,  $\text{C}_8\text{H}_{12}\text{O}_4\text{Cu}$ , for copper suberate, whilst the titration of the acid gave a mean molecular weight of 162; it is suggested that oxidised substances are produced in the bleaching of the wax, which, on hydrolysis, break down into heptaldehyde and lower fatty acids. Pure glycerol was isolated from the aqueous liquors.

The insoluble acids contain a little oleic acid, but consist mainly of palmitic acid, together with a dibasic *japanic acid*,  $\text{C}_{20}\text{H}_{40}(\text{CO}_2\text{H})_2$ .

This can readily be separated from the palmitic acid by adding alcoholic potash to a 10 per cent. alcoholic solution of the fatty acids, draining the less soluble potassium salt at about  $60^{\circ}$  and crystallising the acid from alcohol or chloroform. In this way, the acid is obtained in minute, white flakes and melts at  $117.7-117.9^{\circ}$ . It only absorbs a trace of iodine and is therefore saturated, and contains no hydroxyl group. A molecular weight determination in boiling alcoholic solution gave  $M=364$  and  $365$ , whilst titration gave  $M=186.2 \times n$ . When heated at  $150^{\circ}$ , the acid begins to lose water with partial formation of an anhydride, but when heated at  $200^{\circ}$ , it also loses carbon dioxide and gives a suberone-like ketone,  $C_{20}H_{40}CO$ ; this was separated by extracting with alcoholic potash and crystallising from alcohol, when it was obtained in minute needles melting at  $82-83^{\circ}$ .

The acid probably exists in the wax as a mixed *glyceride* containing 1 mol. palmitic acid and 1 mol. japanic acid; by extracting the fatty acids with alcohol, separating the tripalmitin by crystallising from benzene, and extracting repeatedly with absolute alcohol, a hard mass was obtained which melted at  $43-45^{\circ}$  and had an ether number 252.6, the theory for the *glyceride* being 253.4. T. M. L.

**Substituted Dibasic Acids. Conversion of an Acid Chloride into an Anhydride by the Action of Haloid Acids.** By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1900, i, 404; from *Bull. Acad. roy. Belg.*, [iii], 37, 680-700. Compare *Bull. Acad. roy. Belg.*, [iii], 29, 609).—By the action of bromine and iron on succinic chloride, dibromomaleic anhydride,  $\begin{matrix} \text{CBr} \cdot \text{CO} \\ | \\ \text{CBr} \cdot \text{CO} \end{matrix} > \text{O}$ , is formed; it melts at  $112^{\circ}$

and boils at  $225^{\circ}$ . Barium dibromomaleate,  $C_2Br_2O_4Ba$ , crystallises from water, in which it is easily soluble, in lustrous needles, and is precipitated from its aqueous solution by alcohol. Acetic chloride is completely charred by the action of bromine and iron, and dibromomaleic acid is not formed. Citraconic and mesaconic acids, under similar conditions, yield bromocitraconic anhydride,  $\begin{matrix} \text{CMe} \cdot \text{CO} \\ | \\ \text{CBr} \cdot \text{CO} \end{matrix} > \text{O}$ ,

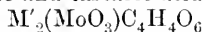
melting at  $98^{\circ}$ . By the prolonged action of chlorine and iron on chlorofumaric chloride, dichloromaleic anhydride and dichloromaleic chloride,  $\text{COCl} \cdot \text{CCl} \cdot \text{CCl} \cdot \text{COCl}$ , are obtained. The former melts at  $119^{\circ}$ . The latter, which may also be prepared by the action of phosphorus pentachloride on dichloromaleic anhydride, forms an oil, has a pungent odour, boils at  $192-194^{\circ}$ , is volatile in steam, and is soluble in organic solvents. Unlike other acid chlorides, it does not fume in the air, and is not decomposed by boiling with water or alkali. It is attacked, however, by alcoholic potassium hydroxide solution.

E. W. W.

**Some Complex Salts of Tartaric and Malic Acids, and their Specific Rotatory Power.** II. By ARTHUR ROSENHEIM and HERMANN ITZIG (*Ber.*, 1900, 33, 707-718. Compare this vol., i, 135).—Boiling concentrated aqueous solutions of normal alkali tartrates dissolve precipitated tungstic acid to form soluble, amorphous "tungstotartrates" of the type  $M'_2(WO_3)_4H_4O_6$ ; the

*potassium* double salt (with  $5\text{H}_2\text{O}$ ) in concentrated solutions (more than 3 grams per 100 c.c.) has  $[\alpha]_D + 340^\circ$  at  $11^\circ$ ; the *sodium* salt (with  $2\text{H}_2\text{O}$ ) has  $[\alpha]_D + 273^\circ$  at  $17^\circ$ ; and the *ammonium* salt (with  $1\text{H}_2\text{O}$ ),  $[\alpha]_D + 296^\circ$  at  $12^\circ$  (compare Landolt's *Optische Drehungsvermögen*, 2nd ed., 220). In dilute solutions, these double salts, unlike the complex beryllium tartrates formerly described (*loc. cit.*), undergo hydrolysis, the specific rotatory power diminishing very greatly; the high rotation in concentrated solution is probably due to the complex  $\text{CO}_2\text{M}'\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CO}_2\cdot\text{WO}_2\cdot\text{OM}'$ . Sodium metatungstate does not increase the specific rotatory power of tartaric acid, but sodium paratungstate has a greater effect than the ordinary tungstate, a maximum value of  $[\alpha]_D + 364\cdot5^\circ$  at  $14^\circ$  being reached when the substances are in the ratio  $1\text{C}_4\text{H}_6\text{O}_6 : \frac{1}{3}\text{Na}_{10}\text{W}_{12}\text{O}_{41}$ .

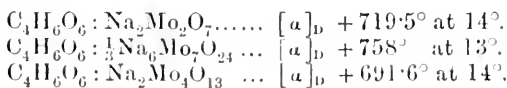
Double salts of molybdic and tartaric acids of the type



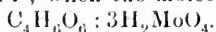
could not be obtained by the interaction of alkali tartrates and molybdic acid, but were prepared by evaporating solutions containing a mixture of the alkali bimolybdate,  $\text{M}'_2\text{Mo}_2\text{O}_7$ , and the alkali hydrogen tartrate; the specific rotatory power of the *potassium* salt (with  $4\text{H}_2\text{O}$ ), and the *sodium*, *lithium*, and *magnesium* double salts (each with  $5\text{H}_2\text{O}$ ), is given in the following table. This also shows the molecular ratio of tartaric acid, and the metallic molybdate in the double salts, and indicates errors formerly made by Gernez (compare *Opt. Drehungsvermögen*, *loc. cit.*) with regard to these ratios.

Molecular ratio.	Authors.	Maximum $[\alpha]_D$ .	Authors.
Gernez.	Gernez.	—	—
—	$1\text{K}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	—	$+ 550\cdot7^\circ$ at $15^\circ$
$1\text{Na}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$1\text{Na}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 517^\circ$ at $17^\circ$	$+ 543\cdot6^\circ$ at $17^\circ$ ( $c = 10\cdot286$ )
$2\text{Li}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$1\text{Li}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 484^\circ$ at $16^\circ$	$+ 489\cdot3^\circ$ at $16^\circ$
$2\text{MgMoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$1\text{MgMoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 523$ at $16^\circ$	$+ 521^\circ$ at $20^\circ$
$\frac{2}{3}(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} : 1\text{C}_4\text{H}_6\text{O}_6$	$\frac{1}{2}(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 781^\circ$ at $17^\circ$	$+ 790^\circ$ at $14^\circ$

All the salts are strongly hydrolysed in dilute solution, so that the specific rotatory power rapidly falls on diluting the concentrated solutions; the rotatory power, however, increases in an extraordinary degree on raising the temperature. The maximum rotatory power of solutions containing tartaric acid and sodium bimolybdate, paramolybdate, and tetramolybdate respectively, corresponds with the following ratios:



The sodium molybdotartrate,  $\text{MoO}_2(\text{NaC}_4\text{H}_4\text{O}_6)_2$ , obtained in solution by the interaction of sodium hydrogen tartrate and molybdic acid (Henderson and Barr, *Trans.*, 1896, 69, 1451), has  $[\alpha]_D 252\cdot3^\circ$  at  $12^\circ$ , which is not changed on diluting. Mixtures of molybdic acid and tartaric acid in solution gave maximum values  $[\alpha]_D + 506^\circ$  at  $17^\circ$ , and  $[\alpha]_D + 498^\circ$  at  $14^\circ$ , when the molecular ratio was



W. A. D.

**Formation of Crystalline Manganese Oxalate by the Oxidation of Citric Acid with Potassium Permanganate.** By GEORGES DENIGES (*J. Pharm.*, 1900, [vi], 11, 102—104. Compare this vol., i, 89).—When citric acid is oxidised with potassium permanganate, the oxalic acid found amongst the oxidation products gradually separates out as crystalline manganese oxalate. Some of the crystals are prismatic and of a rose colour, and correspond with the formula  $\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ; the others are white, hexagonal crystals, and contain only  $2\text{H}_2\text{O}$ .

Crystalline manganese oxalate may also be obtained by the slow double decomposition of a mixture of manganese sulphate and ammonium oxalate, acidified with dilute acetic acid. If the decomposition is effected in the cold, the rose crystals are obtained, whereas, in boiling solution, the white, hexagonal crystals are formed.

H. R. LE S.

**Melting Point of Chloral Hydrate.** By C. G. L. WOLF (*J. Physical Chem.*, 1900, 4, 21—32).—The author has examined the phenomena of fusion of chloral hydrate, and considers that the variations observed in the melting point are not due to the existence of two modifications, but to dissociation, and that only one form of the compound exists in the melted mass, both the forms obtained by Pope (*Trans.*, 1899, 75, 455) giving similar results. The temperature at which the undissociated compound, the dissociation products, and the liquid are in equilibrium is about  $47^\circ$ , but the melting point for the undissociated compound itself is above  $72^\circ$ , at which temperature its vapour pressure is about 22 mm.

L. M. J.

**Molecular Weight of the Aldols.** By LEOPOLD KOHN (*Monatsh.*, 1900, 21, 80—97).—The molecular weights of various aldols and their polymerisation products have been determined by the method of Bleier and Kohn (this vol., ii, 192). It is found that “for each aldol there is a temperature above which only a unimolecular type can exist and below which two different molecular forms can exist, namely, a bimolecular form, which is unstable, and a unimolecular form; the temperature at which the depolymerisation of the double molecule takes place lies near to the boiling point of the aldol under a low pressure.”

The various theoretical considerations do not lend themselves to abstraction.

R. H. P.

**Mesityl Oxide.** By HERMANN PAULY and HANS LIECK (*Ber.*, 1900, 33, 500—504).—*Bromomesityl oxide*,  $\text{C}_6\text{H}_3\text{Br} \cdot \text{CMe}_2$ , obtained by the action of alcoholic potash (1 mol.) on an alcoholic solution of mesityl oxide dibromide (Claisen, this Journ., 1876, i, 985) and subsequent precipitation with water, distils at  $60\text{--}61^\circ$  under 20 mm. pressure, and has a sp. gr.  $1.2832$  at  $11^\circ/4^\circ$ ; it has an extremely irritating action on the mucous membrane, and readily reduces Fehling's solution and silver oxide. Its *dibromide* crystallises in needles melting at  $143^\circ$ . *Mesityl oxide dichloride*,  $\text{CHClAc} \cdot \text{CClMe}_2$ , obtained by saturating an ethereal or alcoholic solution of mesityl oxide with chlorine at low temperatures, is a colourless liquid distilling at  $77^\circ$  under 12 mm.



pressure and having a sp. gr. 1.1942 at 11°/4°. *Chloromesityl oxide* distils at 47° under 12 mm. pressure, decomposes when heated under atmospheric pressure, has a sp. gr. 1.1268 at 11°/4°, and yields a *dichloride* distilling at 104° under 18 mm. pressure. *Methoxymesityl oxide*,  $\text{OMe}\cdot\text{CAc}\cdot\text{CMc}_2$ , distils at 167—168°, and has a sp. gr. 0.9713 at 11°/4°. *Acetoxymesityl oxide*,  $\text{OAc}\cdot\text{CAc}\cdot\text{CMc}_2$ , is a colourless liquid distilling at 74° under 12 mm. pressure, and at 177° at atmospheric pressure; it has a sp. gr. 0.9139 at 11°/4°; when boiled for 2—3 hours with 10 per cent. sulphuric acid, it yields Otte and Pechmann's methyl isopropyl diketone (Abstr., 1889, 1137), the *osazone* of which crystallises in sulphur-yellow needles melting at 117°. Methyl isopropyl diketone and *o*-phenylenediamine yield

*methylisopropylquinoxaline*,  $\text{C}_8\text{H}_4\begin{smallmatrix} \text{N}:\text{CMe} \\ \text{N}:\text{C}\cdot\text{CHMe}_2 \end{smallmatrix}$ , which crystallises in plates, melts at 37°, and distils at 264°. Bromomesityl oxide and the sodium derivative of ethyl malonate react but slowly with one another; when they are heated in alcoholic solution for some 70 hours, a 17 per cent. yield of *ethyl mesityl-oxide-malonate* [ $\beta$ -*acetyliso*- $\Delta^8$ -*pentene- $\alpha$ -dicarboxylate*],  $\text{CMc}_2\cdot\text{CAc}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , is obtained; this distils at 141° under 19 mm. pressure and has a sp. gr. = 1.064 at 11°/4°. *Ethyl  $\alpha\beta$ -diacetylpyroterebic acid*,  $\text{CMc}_2\cdot\text{CAc}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , distils at 132° under 18 mm. pressure, and gives an indigo-blue coloration with ferric chloride.

J. J. S.

**Methyl-2-heptene-4-one-6 and the Synthesis of an Aliphatic Isogeranic Acid.** By FERDINAND TIEMANN (*Ber.*, 1900, 33, 559—566).— $\alpha$ -Isomethylhepteneone ( $\beta$ -methyl- $\Delta^7$ -heptene- $\zeta$ -one) has been described by Barbier and Bouveault (Abstr., 1894, i, 224) and Léser (Abstr., 1898, i, 512). It is best purified by conversion into the sodium hydrosulphonate and after this treatment boils at 178—180° (corr.), and has a sp. gr. 0.8443 at 17°, and a refractive index  $n_D$  1.44275. It forms a semicarbazone melting at 113°. The second carbazone, described by Léser as melting at 100°, is probably a mixture of this with some impurity. The *disemicarbazone*,  $\text{C}_{10}\text{H}_{22}\text{O}_2\text{N}_6$ , melts at 182°.

When oxidised first with potassium permanganate and then with chromic acid, it yields isovaleric acid, so that the constitution assigned to the compound by Barbier and Bouveault is confirmed. When it is treated with ethylbromoacetate and zinc, *ethylhydroxydihydroisogeranate*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is formed, which boils at 125—135° under 20 mm. pressure. It has a sp. gr. 0.9385 at 17°, and a refractive index  $n_D$  1.45579. When the free acid is distilled in a vacuum, *isogeraniolene*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CMe}:\text{CH}_2$ , and *isogeranic acid*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CMe}:\text{CH}\cdot\text{CO}_2\text{H}$ , are produced. Isogeraniolene boils at 140—142°, and has a sp. gr. 0.7610 at 17° and a refractive index  $n_D$  1.45409. Isogeranic acid boils at 151—154° under a pressure of 14 mm., and has a sp. gr. 0.959 at 17°, and a refractive index  $n_D$  1.49194. On oxidation with potassium permanganate, followed by chromic acid, it yields isovaleric acid.

A. H.

**Electro-synthesis of Diketones and Ketones.** By HANS HOFER (*Ber.*, 1900, 33, 650—657).—The chief product of the electrolysis of aqueous potassium pyruvate is acetic acid, small quantities of

diacetyl also being formed and carbon dioxide evolved. Potassium laevulate gives rise to  $\alpha\delta$ -diacetylbutane in about 50 per cent. of the theoretical yield, a quantity of acetic acid being also produced. From a mixture of potassium pyruvate (1 mol.) and acetate (3 mols.), the products obtained are diacetyl and acetone. Potassium pyruvate and butyrate together yield methyl propyl ketone, which is also obtained from a mixture of potassium laevulate and acetate. A small quantity of  $\alpha\beta$ -diacetyethane is formed on electrolysing a mixture of aqueous solutions of potassium pyruvate and laevulate. T. H. P.

**Acetylacetone.** By FRIEDRICH GACH (*Monatsh.*, 1900, 21, 98—117).—The following new metallic salts of acetylacetone were prepared and analysed:— $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2 + \text{C}_2\text{H}_5\text{OH}$ ;  $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$ ;  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ ;  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$ ;  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2 + \text{C}_2\text{H}_5\text{OH}$ ;  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2 + \text{COMe}_2$ ;  $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ ;  $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3$ ;  $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$ ;  $\text{Mo}(\text{C}_5\text{H}_7\text{O}_2)_2$ . All those which crystallise free from the solvent can be sublimed without decomposition, and their vapour densities were determined by Bleier and Kohn's method (this vol., ii, 192). R. H. P.

**Determination of the Inverting Power of Raw Sugar.** By LEOPOLD JESSER (*Chem. Centr.*, 1900, i, 106—107; from *Oesterr. Zeit. Zuck.-Ind. Landw.*, 28, 626—628).—The amount of sugar which is decomposed when neutral or alkaline aqueous solutions of raw sugar are boiled, was determined by a method which depends on the property of invert sugar of forming acids of constant acidity when boiled with alkalis and then with excess of acid. The data obtained showed that more sugar is decomposed in alkaline than in neutral solutions. Since the results may not only be affected by the presence of organic compounds having inverting properties, but also by the fact that titration does not necessarily indicate the amount of alkali contained in the product, the amount of sugar inverted was determined by ascertaining its alkalinity before and after boiling for two hours. The difference gives the amount of alkali which is neutralised by the acids formed by boiling the sugar, and those also formed from the invert sugar. From the results, the quantity of invert sugar and of sucrose which has been decomposed can be calculated (compare *Oesterr. Zeit. Zuck.-Ind. Landw.*, 27, 35). The results are tabulated in the original paper, and show that the amount of sugar decomposed differs with the various samples, and bears no relation to the alkalinity. The alkalinity of a raw sugar is therefore neither a criterion of its purity nor of the amount of alkali present. Generally speaking, the amount of sugar decomposed in the case of the crude products was not very different from that obtained in the case of pure sucrose, and in two cases, in which the sugars were distinctly alkaline to phenolphthalein and litmus, the solutions, on boiling, behaved like neutral solutions. Although the purified products showed a marked alkalinity, the amount of sugar decomposed was double that of the crude sugars under similar conditions. One sample of crude sugar, however, gave a result similar to those obtained with purified sugars. The higher inverting powers of the latter must be due to the presence, not only of inverting substances normally contained in the sugar, but also to others formed in the process of manufacture, and possibly by overheating. E. W. W.

Is the Diminution of the Rate of Inversion caused by the Presence of Normal Salts of Inverting Acids, due to the Formation of Esters? By F. STOLLE (*Chem. Centr.*, 1900, i, 439; from *Zeit. Ver. Rübenzuck-Ind.*, 1899, 941—951).—In the action of oxalic acid on raw sugar, as the temperature is raised, each rise of  $5^{\circ}$  from  $5^{\circ}$  to  $50^{\circ}$  causes twice the quantity of sugar to be inverted, but above  $50^{\circ}$  the increase becomes less. The inverting power and rapidity of action of the equivalent weight of oxalic acid is equal, or nearly equal, to that of the molecular weight of the potassium hydrogen oxalate. When a mixture of equivalent weights of oxalic acid and normal potassium oxalate is used, potassium hydrogen oxalate is not formed, but probably an ester, and it is the presence of this compound which determines the diminution of the rapidity of inversion.

E. W. W.

Colouring Matters contained in "Sugar-Colours," and their Detection. By RUDOLF SCHWEITZER (*Chem. Centr.*, 1900, i, 491; from *Zeit. ges. Brauw.*, 23, 46—48).—The commercial "sugar-colour" preparations differ in their behaviour towards acetic acid and lead acetate; all those prepared by means of alkalis give deep brown precipitates which dissolve in sodium hydroxide solution, forming brown solutions, whilst others are not precipitated, or form only very slight precipitates. A substance, *alkaramel*,  $C_{12}H_{11}O_4$ , having the properties of an acid, was isolated from caramel, prepared by heating raw sugar with 10 per cent. of sodium carbonate, by precipitating the acetic acid solution with lead acetate and removing the lead from the precipitate. It is a brown powder, leaves no ash, is slightly soluble in dilute alcohol, almost insoluble in water, insoluble in organic solvents, and easily soluble in ammonia or alkalis. Pure sugar-colouring materials, malt extracts, and uncoloured beers do not contain *alkaramel*, but it is characteristic of all alkaline colouring preparations. It has been detected in some beers.

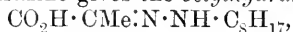
E. W. W.

Action of Silver Oxide and of Hydroxylamine on Bromoamines. By NIC. M. KJNER (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 872—901, and 948).— $\gamma$ -Amino-n-heptane,  $NH_2 \cdot CHPr^a$ , obtained by the reduction of dipropylketoxime with metallic sodium, boils at  $140$ — $141^{\circ}$  under 745 mm. pressure, and has a sp. gr.  $0.7671$  at  $20^{\circ}/0^{\circ}$ . The *hydrochloride* forms thin, prismatic crystals melting at  $247^{\circ}$ , and the *platinichloride* crystallises in anhydrous, golden leaflets. The amine combines with phenylthiocarbimide, forming the corresponding *thiocarbamilide*,  $NHPh \cdot CS \cdot NH \cdot C_7H_{15}$ , which crystallises in needles melting at  $75^{\circ}$ .

On brominating the amine and acting on the product with silver oxide, the *heptylhydrazine*,  $N_2H_3 \cdot CHPr^a$ , is formed; it boils undecomposed at  $190$ — $192^{\circ}$  under the ordinary pressure, and has a sp. gr.  $0.8545$  at  $0^{\circ}/0^{\circ}$ . It quickly oxidises in the air with evolution of gas, and reduces an ammoniacal solution of silver oxide in the cold. With pyruvic acid, it yields the *heptylhydrazone*,  $CO_2H \cdot CMc \cdot N_2H \cdot C_7H_{15}$ , which is readily soluble in benzene and in light petroleum, from which it separates in slender needles melting at  $57$ — $58^{\circ}$ ; it is readily soluble in alkalis, and is reprecipitated unchanged on the addition of acids. The hydrazine combines with phenylthiocarbimide, yielding the *thio-*

*carbanilide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_7\text{H}_{15}$ , which separates from alcohol in beautiful plates melting at  $122^\circ$ .

By reducing methyl hexyl ketone oxime, or by the action of ammonium formate on methyl hexyl ketone,  $\beta$ -amino-octane is obtained; it boils at  $165\text{--}166^\circ$  under 758 mm. pressure, and has a sp. gr. 0.7721 at  $20^\circ/0^\circ$ . Jahn gave the boiling point  $162.5^\circ$ , and Konowaloff found that it boils at  $163\text{--}164^\circ$  under 754 mm. pressure, and has a sp. gr. 0.7745 at  $20^\circ/0^\circ$ . Along with the octylamine obtained by the second of the above methods, there is found a small quantity of *dioctylamine*,  $\text{NH}(\text{C}_8\text{H}_{17})_2$ , which boils at  $281.5^\circ$  under 739 mm. pressure, and has the sp. gr. 0.7948 at  $20^\circ/0^\circ$ ; by the action of sodium nitrite on its hydrochloride, the *nitroso*-compound,  $\text{NO}\cdot\text{N}(\text{C}_8\text{H}_{17})_2$ , is obtained. By the action of silver oxide on the bromo-derivative of  $\beta$ -amino-octane, *methyl hexyl ketone octylhydrazone*,  $\text{C}_8\text{H}_{16}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_8\text{H}_{17}$ , and *octylhydrazine*,  $\text{CH}_3\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CHMe}\cdot\text{NH}\cdot\text{NH}_2$ , are formed; the latter boils at  $210\text{--}215^\circ$ , oxidises in the air with evolution of gas, and, on gently warming, reduces an ammoniacal solution of silver oxide. The octylhydrazine combines with phenylthiocarbimide, yielding the corresponding *thiocarbanilide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_8\text{H}_{17}$ , which crystallises from ethyl acetate in slender needles melting at  $116^\circ$ . With pyruvic acid, octylhydrazine gives the *octylhydrazone*,



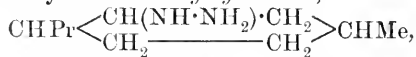
which melts at  $39^\circ$ .

The interaction of silver oxide and 1-methyl-3-bromoaminocyclohexane yields 1:3-methylcyclohexenone and a small quantity of 1:3-methylcyclohexylhydrazine, which gives a *thiocarbanilide*,



crystallising from alcohol in colourless, rhombic plates melting at  $137\text{--}138^\circ$ .

Silver oxide reacts with *l*-bromomenthylamine, forming menthanementhylhydrazone, which melts at  $93^\circ$  and in benzene solution has a specific rotation  $[\alpha]_D = -378.1^\circ$ . When boiled with hydrochloric acid, this hydrazone yields *l*-menthylhydrazone,



which is a thick, colourless liquid boiling at  $240\text{--}242^\circ$  under 761 mm. pressure; it oxidises in the air with evolution of gas. With phenylthiocarbimide, it yields *menthylhydrazylphenylthiocarbanilide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{19}$ , melting at  $160^\circ$ ; this is insoluble in alkalis, and in benzene solution has the specific rotation  $[\alpha]_D = -49.10^\circ$ .

Concentrated nitric acid oxidises menthanementhylhydrazone at the ordinary temperature, yielding a substance,  $(\text{C}_{20}\text{H}_{38}\text{ON}_2)$ , probably  $\text{ON}_2(\text{C}_6\text{H}_9\text{MePr})_2$ , which crystallises from aqueous alcohol in slender, colourless, silky needles, melts at  $84\text{--}84.5^\circ$ , is readily volatile in a current of steam, has the normal molecular weight in freezing benzene, and in benzene solution has a specific rotation  $[\alpha]_D = -177^\circ$  at  $22^\circ$ . When heated with hydrochloric acid, it is resolved into hydrazine and menthone, and with concentrated hydriodic acid it yields menthyl iodide and a menthylamine salt. Zinc dust in dilute aqueous solution reduces it to menthanementhylhydrazone, which has a specific rotation  $[\alpha]_D = -406^\circ$ , a value considerably higher than that ( $-378.1^\circ$ ) of the original substance.

*Dimenthylamine*,  $\text{NH}(\text{C}_{10}\text{H}_{19})_2$ , obtained together with *d*-menthylamine when ammonium formate is heated with menthone, is a thick liquid with a faint smell; it boils at  $220\text{--}222^\circ$  under 45 mm. pressure, and at the ordinary pressure distils almost unchanged at above  $300^\circ$ . The hydrochloride gives with potassium nitrite a liquid *nitrosamine*. *d*-Menthylamine boils at  $206^\circ$ , has the sp. gr. 0.8589 at  $20^\circ/0^\circ$ , and the specific rotation  $[\alpha]_D = +14.87^\circ$  (Wallach gives  $14.71^\circ$ ). The action of silver oxide on the bromo-derivative of *d*-menthylamine yields menthone and *menthazine*,  $\text{N}_2(\text{C}_6\text{H}_8\text{MePr})_2$ , which crystallises from aqueous alcohol in pale yellow needles melting at  $50\text{--}52^\circ$ ; it is also obtained on warming menthone with hydrazine hydrate and anhydrous barium oxide. On warming with dilute hydrochloric acid, it yields hydrazine hydrochloride. T. H. P.

**Some Halogen Derivatives of Hexamethylenetetramine (Urotropine).** By M. HÖHNEL (*Arch. Pharm.*, 1899, 237, 692—698).—The following crystalline derivatives of hexamethylenetetramine were prepared by mixing the base, or a derivative of it, with the halogen, &c., usually in alcoholic, but sometimes in chloroform or aqueous, solution. The perhaloids tend to lose the excess of halogen in the air.

*Perbromide*,  $(\text{CH}_2)_6\text{N}_4\text{Br}_4$ . *Methobromide dibromide*,  $(\text{CH}_2)_6\text{N}_4\text{EtBr}_2\text{Br}_2$ . *Diiodide*,  $(\text{CH}_2)_6\text{N}_4\text{I}_2$ . *Periodide*,  $(\text{CH}_2)_6\text{N}_4\text{I}_4$ . *Methiodide diiodide*,  $(\text{CH}_2)_6\text{N}_4\text{MeI}_2\text{I}_2$ . *Hydriodide diiodide*,  $(\text{CH}_2)_6\text{N}_4\text{HI}_2\text{I}_2$ . *Diiodide mercuriiodide*,  $(\text{CH}_2)_6\text{N}_4\text{I}_2 + 2\text{HgI}_2$ ; *diiodide mercurichloride*,  $(\text{CH}_2)_6\text{N}_4\text{I}_2 + 2\text{HgCl}_2$ . *Chloriiodide*,  $(\text{CH}_2)_6\text{N}_4\text{ICl}$ . *Chloral*,  $(\text{CH}_2)_6\text{N}_4 + \text{CCl}_3\cdot\text{CHO} + 2\text{H}_2\text{O}$  (compare German Patent, 87933). *Bromal*,  $(\text{CH}_2)_6\text{N}_4 + \text{CBr}_3\cdot\text{CHO} + 2\text{H}_2\text{O}$ . C. F. B.

**Polyaspartic Acids.** By HUGO SCHIFF (*Gazzetta*, 1900, 30, i, 8—25; and *Annalen*, 1900, 310, 301—305. Compare Abstr., 1899, i, 195 and 674).—[With GIULIO MARZICHI.]—When octoaspartide is heated with ammonia in ethereal solution in sealed tubes at  $100^\circ$ , *octoaspartotetramide*,  $\text{C}_{32}\text{H}_{26}\text{O}_{17}\text{N}_8 + 4\text{NH}_3$ , is obtained as a yellowish powder; heated at  $120^\circ$  or placed in a vacuum over sulphuric acid, it loses ammonia and yields the triamide. The latter neutralises rather more than 2 mols. of potash and gives two copper compounds, having the composition  $\text{C}_{32}\text{H}_{11}\text{O}_{22}\text{N}_{11}\text{Cu}_2$  and  $\text{C}_{32}\text{H}_{35}\text{O}_{27}\text{N}_{11}\text{Cu}_5$  respectively.

Tetra-aspartide loses all its water at  $120\text{--}130^\circ$ , and at a higher temperature yields *diaspartilodiaspartic acid*,  $\text{C}_{16}\text{H}_{18}\text{O}_{11}\text{N}_4$ , which absorbs ammonia with development of heat, forming a *tetrammonium* salt,  $\text{C}_{16}\text{H}_{18}\text{O}_{11}\text{N}_4 + 4\text{NH}_3$ , and this, when placed in a vacuum over sulphuric acid and finally heated at  $120^\circ$ , gives the *diammonium* salt,  $\text{C}_{16}\text{H}_{18}\text{O}_{11}\text{N}_4 + 2\text{NH}_3$ . The latter is soluble in water, giving a neutral solution, from which it is precipitated by the addition of acetic acid; on heating the solution for some time, it becomes acid, and on then evaporating in a vacuum it deposits an almost colourless, glassy, and slightly hygroscopic compound of the composition  $\text{C}_{16}\text{H}_{22}\text{O}_{12}\text{N}_4 + 2\text{NH}_3$ , which dissolves in water, and is not precipitated by acetic acid.

On heating ammonium tetra-aspartate at  $200\text{--}210^\circ$ , it loses all its ammonia and is converted into octoaspartide.

[With MARIO BETTI.]—*Diisoamylamineoctoaspartide*,  $C_{32}H_{26}O_{17}N_8 + 2C_5H_{13}N$ , has a yellowish colour, and is insoluble in all solvents. *Hexa isoamylamineoctoaspartide*,  $C_{32}H_{26}O_{17}N_8 + 6C_5H_{13}N$ , is a yellowish substance which partially dissolves in concentrated potassium hydroxide solution, giving an odour of isoamylamine; after standing for some time, this solution gives the biuret reaction. It is slightly soluble in ammonia and partially so in dilute acetic acid. *Hepta isoamylamineoctoaspartide*,  $C_{32}H_{26}O_{17}N_8 + 7C_5H_{13}N$ , has an almost white, crystalline appearance, and with potash gives an odour of isoamylamine, and, after a time, the biuret reaction; it is insoluble in the ordinary solvents and partially melts at about  $220^\circ$ .

*Tetrabenzylamineoctoaspartide*,  $C_{32}H_{26}O_{17}N_8 + 4C_7H_9N$ , is a yellow substance which does not melt; it is fairly soluble in cold potash solution or hot ammonia solution, and gives the biuret reaction. *Octobenzylamineoctoaspartide* has a yellow colour and dissolves slightly in potash, the solution giving a faint biuret reaction; it is almost insoluble in alcohol or dilute acids; fusion commences at  $205^\circ$ , but is never complete.

*Tetra-m-tolylenediamineoctoaspartide*,  $C_{32}H_{26}O_{17}N_8 + 4C_7H_{10}N_2$ , is a brownish-yellow, amorphous substance slightly soluble in acetic acid or potash, the colour of the solution not allowing the biuret reaction to be detected; when the solution is warmed with potash, ammonia is evolved, and when treated with furfuraldehyde and acetic acid, an orange-red coloration is produced, indicating the presence of free aromatic amino-groups; it softens at  $250^\circ$ , and, at higher temperatures, decomposes. It yields two *copper* compounds; the first, having the composition  $C_{60}H_{72}O_{23}N_{16}Cu_3$ , is a greyish-green substance, and the other,  $C_{60}H_{70}O_{21}N_{16}Cu_2$ , has a green colour and darkens and decomposes at above  $200^\circ$ .

*Dibenzidineoctoaspartide*,  $C_{32}H_{26}O_{17}N_8 + 2C_{12}H_{12}N_2$ , is resinified by acids or potash, dissolves slightly in ammonia solution, and gives the biuret reaction. *Tribenzidineoctoaspartide* gives the biuret reaction, and answers to the test for free aromatic amino-groups; it is slightly soluble in ammonia or dilute potash solution, but insoluble in boiling concentrated hydrochloric acid, and at high temperatures decomposes without melting. It forms a yellowish-green *copper* salt of the composition  $C_{68}H_{80}O_{31}N_{14}Cu_5$ . *Pentabenzidineoctoaspartide* does not melt, and is insoluble in potash or hydrochloric acid. By treating the tribenzidine derivative with a further quantity of benzidine, a compound of the composition  $C_{32}H_{26}O_{17}N_8 + 5C_{12}H_{12}N_2 - 4NH_3$  is obtained.

With  $\beta$ -naphthylamine, octoaspartide gives *tetranaphthyl-octonaphthylamineoctoaspartide*,  $C_{32}H_{26}O_{17}N_8 + 12C_{10}H_9N - 4NH_3$ , which is obtained in yellowish flocks by pouring its alcoholic solution into a large volume of very dilute hydrochloric acid; it melts sharply at  $165-166^\circ$  and is soluble in potash, but does not give the biuret reaction. T. H. P.

**Preparation of Carbamide from Guanidine.** By HUGO FLEMING (*Chem. Zeit.*, 1900, 24, 56).—Carbamide may be readily obtained in a pure state by the action of barium hydroxide on the boiling aqueous solution of a guanidine salt, as first suggested by Baumann (*Ber.*, 1873, 6, 1376). E. G.

**Pentabromobenzene.** By PAUL JACOBSON and ARTHUR LOEB (*Ber.*, 1900, 33, 702—706).—Pentabromoaniline sinters at  $254^{\circ}$ , melts at  $256$ — $257^{\circ}$  ( $261$ — $262^{\circ}$ , corr.), not at  $225^{\circ}$ , as stated by Hantzsch and Smythe (*Ber.*, 1900, 33, 505), and by elimination of the amino-group yields pentabromobenzene, which melts at  $159$ — $160^{\circ}$  (Hantzsch and Smythe,  $158^{\circ}$ ). Neither Kekulé (*Annalen*, 1866, 137, 171), Bässmann (*Annalen*, 1878, 191, 208), nor Diehl (*Ber.*, 1878, 11, 191), who have described pentabromobenzene as melting above  $240^{\circ}$ , were dealing with the true substance; that obtained by the authors on nitration yields *pentabromonitrobenzene*, which crystallises from alcohol in white needles melting at  $234$ — $235^{\circ}$  (corr.) (Jackson and Bancroft, *Abstr.*, 1890, 982, describe “pentabromonitrobenzene” as melting at  $248^{\circ}$ ), and on reduction with iron and acetic acid yields pentabromoaniline. Two of the bromine atoms of pentabromobenzene are removed on warming with alcoholic sodium ethoxide. W. A. D.

**Oxidation of Aromatic Iodides.** By EUGEN BAMBERGER and ADOLF HILL (*Ber.*, 1900, 33, 533—536).—Caro's reagent (*Zeit. angew. Chem.*, 1898, 845) oxidises aliphatic amines of the type  $R \cdot CH_2 \cdot NH_2$  to the corresponding oximes,  $R \cdot CH : N \cdot OH$ ,  $\beta$ -alkylhydroxylamines probably being formed initially; methylamine yields formoxime and benzylamine *syn*- and *anti*-benzaloximes. Details of this work will be published later.

The same reagent oxidises aromatic iodides,  $C_6H_4R \cdot I$ , to the corresponding iodoxy-compounds,  $C_6H_4R \cdot IO_2$ ; in the present paper, the oxidation of iodobenzene, and *o*-, *m*-, and *p*-iodotoluene is dealt with. *m*-Iodoxytoluene,  $C_7H_7O_2I$ , the only new compound described, crystallises in white, lustrous needles, explodes between  $214^{\circ}$  and  $221^{\circ}$ , and is converted by hydrogen peroxide into *m*-iodotoluene (compare Willgerodt, *Abstr.*, 1893, i, 505). W. A. D.

**Gradual Electrolytic Reduction of Nitrobenzene with Limited Cathode Potential.** By FRITZ HABER (*Zeit. Elektrochem.*, 1898, 4, 506—513).—Besides current strength, duration of current, and nature of the electrodes, the fall of potential at the electrodes is an important factor in electrolytic oxidation and reduction processes. A platinum electrode in an alkaline alcoholic solution of nitrobenzene shows the potential difference  $-0.72$  volt; with cathode polarisation, this falls to the value  $-1.29$  volts, when hydrogen is liberated. By regulating the potential difference between these values, various grades of reducing energy are available.

With a potential greater than  $-0.93$  volt, the chief reduction product of nitrobenzene is azoxybenzene, accompanied by small quantities of azobenzene, hydrazobenzene, and aniline. Special experiments showed that hydrazobenzene in alkaline alcoholic solution is further reduced only with great difficulty, and the author accordingly regards the direct line of reduction as being  $C_6H_5 \cdot NO_2 \rightarrow C_6H_5 \cdot NO \rightarrow C_6H_5 \cdot NH \cdot OH \rightarrow C_6H_5 \cdot NH_2$ , the nitrosobenzene and the phenylhydroxylamine reacting to form azoxybenzene. The presence of nitrosobenzene was confirmed: that it cannot be isolated in quantity is due to the fact that the potential difference between platinum and an alkaline alcoholic solution of nitrosobenzene is only  $-0.48$  volt. The hydrazo-

benzene obtained appears to be the reduction product of the secondarily formed azoxybenzene.

The reduction of nitrobenzene in acid alcoholic solution leads to the products azoxybenzene, benzidine, aniline, *p*-aminophenol, and phenetidine; the presence of the two latter compounds points to an intermediate formation of phenylhydroxylamine, which by mere standing in acid alcoholic solution yields phenetidine. The benzidine is formed as the reduction product, not of the phenylhydroxylamine, but of the azoxybenzene; the formation of this compound from nitrosobenzene and phenylhydroxylamine takes place in acid alcoholic solution with much less rapidity than in alkaline alcoholic solution.

The nature of the whole process depends on the energy of reduction as determined by the cathode potential, and on the velocity of the secondary chemical reactions involved. J. C. P.

**Electrolytic Reduction of Nitrobenzene.** By FRITZ HABER and CARL SCHMIDT (*Zeit. physikal. Chem.*, 1900, 32, 271—287).—The results obtained by Haber (see previous abstract) are confirmed and supplemented.

Phenylhydroxylamine cannot be obtained from caustic alkali solutions, owing to its instability in that medium, but it is readily isolated by the electrolytic reduction of nitrobenzene in ammoniacal alcoholic solution. The azobenzene previously detected in the reduction of nitrobenzene in alkaline alcoholic solution is not due to the reduction of the azoxybenzene, but is formed by the action of nitrobenzene on hydrazobenzene.

The authors also discuss Möller's observation (*Abstr.*, 1900, i, 27), that phenylcarbylamine is produced in the electrolysis of alkaline alcoholic solutions of nitrobenzene, and point to the possibility of its being formed from the products at the cathode. J. C. P.

**Benzenesulphonamides of Primary Bases, and the Use of Hinsberg's Reaction for Determination of Structure.** By PAUL DUDEN (*Ber.*, 1900, 33, 477—481).—Whilst benzenesulphonethylamide is dissolved to the extent of 82 per cent. by one equivalent of *N* sodium hydroxide, and to the extent of 94 per cent. by 3 mols., benzenesulphonheptylamide and benzenesulphoncamphylamide are not acted on by alkalis, except in concentrated solutions, when they are converted into the slightly soluble sodium salts; almost the whole of the latter amides can, however, be recovered by extracting the alkaline solution with ether, and these amides are therefore practically neutral substances when compared with the benzenesulphonamides from methylamine, aniline, &c.; it is suggested that perhaps they are 'pseudo-acids,'  $C_6H_5 \cdot SO_2 \cdot NHR$ , which are converted into true acids,  $C_6H_5 \cdot SO(OH) \cdot NR$ , by strong alkali. The author concludes that Hinsberg's reaction cannot be trusted in determining the constitution of bases. T. M. L.

**1-Naphthyliodochloride, 1-Iodosonaphthalene, 4:4'-Diiodo-1:1'-dinaphthyl, 1-Naphthylphenyliodonium Hydroxide and Derivatives thereof.** By CONRAD WILLGERODT and PETER SCHLÖSSER (*Ber.*, 1900, 33, 692—702).—1-Naphthyliodochloride (*Abstr.*, 1894, i, 295),  $C_{10}H_7ICl_2$ , prepared by passing chlorine into a well-cooled



solution of 1-iodonaphthalene in glacial acetic acid or ether, or by dissolving 1-iodosonaphthalene in dilute hydrochloric acid, separates in long, well-formed needles, and rapidly decomposes; the products obtained by the first method are the more unstable, decomposing at  $34^{\circ}$  or  $49^{\circ}$  respectively, according to the solvent used in the preparation, whilst that obtained from 1-iodosonaphthalene decomposes at  $56^{\circ}$ , or after being kept for about 20 hours. In chloroform solution, the decomposition yields iodine, 1-chloronaphthalene tetrachloride, and 1:4-chloriodonaphthalene; the latter is a pale yellow oil which boils above  $300^{\circ}$ , is more stable than 1-iodonaphthalene, and with chlorine yields an unstable *iodochloride* convertible by sodium hydroxide into a moderately stable iodoso-compound.

1-Iodosonaphthalene (*loc. cit.*), when dissolved in glacial acetic acid, yields the *acetate*,  $C_{10}H_7 \cdot I(OAc)_2$ , which separates in short, white needles and decomposes at  $192^{\circ}$  (corr.).

The *basic nitrate*,  $C_{10}H_7 \cdot I(OH)NO_3$ , prepared from 1-iodosonaphthalene and dilute nitric acid, is decomposed by all solvents except chloroform; from the latter, it separates in slender, yellow needles which decompose at  $94^{\circ}$ . The *basic sulphate*,  $(C_{10}H_7 \cdot I \cdot OH)_2SO_4$ , is unstable, decomposing explosively. 1-Iodosonaphthalene in contact with water at the ordinary temperature or with steam yields 1-iodonaphthalene, iodic acid, and probably a hydrocarbon(? a dinaphthyl). Neither 1-iodoxy-naphthalene nor 1:1-dinaphthylidonium iodide could be prepared.

When the foregoing basic sulphate is heated with either glacial acetic acid or chloroform at  $37^{\circ}$ , vigorous action occurs and 4:4'-diiodo-1:1'-dinaphthyl is formed; this crystallises in lustrous prisms, melts at  $238.6^{\circ}$  (corr.), and on reduction with sodium amalgam in absolute alcohol yields *aa*-dinaphthyl (m. p.  $160.5^{\circ}$  corr.). When 1-iodosonaphthalene is dissolved in well-cooled concentrated sulphuric acid, practically none of the expected iodonium compound is formed, the principal product being 4:4'-diiodo-1:1'-dinaphthyl; phosphoric oxide acts similarly. The *iodo-iodochloride*,  $C_{20}H_{12} \cdot I \cdot ICl_2$ , prepared from 4:4'-diiodo-1:1'-dinaphthyl by the action of chlorine, is a yellow, amorphous powder which does not decompose at a definite temperature; the compound  $(C_{10}H_6 \cdot ICl_2)_2$  crystallises from chloroform in beautiful, long needles and decomposes at  $124^{\circ}$ .

*Phenyl- $\alpha$ -naphthylidonium hydroxide*,  $C_{10}H_7 \cdot IPh \cdot OH$ , cannot be prepared by Victor Meyer's method from 1-iodosonaphthalene, iodoxybenzene and moist silver oxide, but is obtained from its chloride; it exists only in aqueous solution, to which it imparts strongly alkaline properties. The *chloride*,  $C_{10}H_7 \cdot IPh \cdot Cl$ , crystallises from water in slender, white needles, and melts at  $168^{\circ}$ ; the corresponding *bromide* is similar and melts at  $179^{\circ}$ , whilst the *iodide* is very sparingly soluble in water, and forms slender, yellow needles which explode at  $176^{\circ}$ . The crystalline *nitrate*,  $C_{10}H_7 \cdot IPh \cdot NO_3$ , decomposes at  $187$ – $188^{\circ}$ ; the *platinichloride*, at  $145$ – $150^{\circ}$ ; whilst the *mercurichloride* melts at  $145^{\circ}$ .

W. A. D.

**Synthesis of Homologues of Diphenylmethane by Oxidation of Toluene and its Homologues.** By MAX WEILER (*Ber.*, 1900, 33, 464–471).—On oxidising toluene with manganese dioxide

and a mixture of sulphuric and acetic acids, a mixture of products results. The fraction boiling from 130—270° contains a little benzaldehyde, but consists chiefly of benzyl acetate. The fraction boiling at 270—300°, when oxidised with chromyl chloride, gives a little anthracene, indicating the presence of dihydroanthracene in the original oil, but chiefly a ketonic mixture of phenyl *p*-tolyl ketone, with an oil which is shown to contain a considerable amount of phenyl *o*-tolyl ketone, since it gives anthraquinone when oxidised with lead oxide; dibenzyl is not present in the original oil, since this would have been isolated from the oxidation product as dibenzyl, stilbene, or benzaldehyde. On oxidation with potassium permanganate, the same fraction gives benzoic, terephthalic, *o*-phthalic, and *p*- and *o*-benzoylbenzoic acids, but not *pp*-diphenyldicarboxylic acid, showing that *pp*-ditolyl is not present in the original oil.

Oxidation of mesitylene with manganese dioxide and sulphuric acid (62 per cent.) gave *s*-dimethylbenzaldehyde (about 31 per cent. of the theoretical amount), mesitylenic acid (3 per cent.), a hydrocarbon melting at 132—133° (0.9 per cent.), pentamethyldiphenylmethane (11.5 per cent.), and higher hydrocarbons. With manganese dioxide, sulphuric and acetic acids, there were produced traces of *s*-dimethylbenzaldehyde, pentamethyldiphenylmethane (13.6 per cent. of theoretical), the hydrocarbon melting at 132—133°, and higher hydrocarbons, but no *s*-dimethylbenzyl alcohol. The hydrocarbon, melting at 132—133°, crystallises in square plates or in four-sided prisms, boils undecomposed at 350°, does not combine with picric acid, is not attacked by ferric chloride, but is oxidised completely by chromic acid, and does not give fluorescent solutions; it is probably 1:3:5:7-tetramethyldihydroanthracene, corresponding with the dihydroanthracene formed in the oxidation of toluene.

T. M. L.

**New Aromatic Hydrocarbon,  $C_{24}H_{18}$ , from Mineral Oil.** By JOSEF KLAUDY and ISIDOR FINK (*Monatsh.*, 1900, 21 118—136).—The authors have isolated a new aromatic hydrocarbon,  $C_{24}H_{18}$ , which they name *crackene*, from the so-called red pitch, which is obtained as a sticky sublimate when the distillation of Saxon lignite tar is conducted at a high temperature. After some months, this sublimate becomes hard, and by crystallisation from benzene or ethyl acetate, yielded the hydrocarbon in the form of yellow leaflets with a green fluorescence; it melts at 308°, can be sublimed, and boils with decomposition at about 500°.

*Dibromocrackene*,  $C_{24}H_{16}Br_2$ , obtained by the action of bromine dissolved in chloroform on crackene, forms small, dark yellow leaflets melting at 141°. Chromic acid oxidises the hydrocarbon to *crackenequinone*, which forms dark red, microscopic crystals melting at 208°, and is probably an *o*-diketone. *Dinitrocrackene* is a dark red powder, and *tetranitrocrackene* a bright yellow powder, which melts and explodes below 100°.

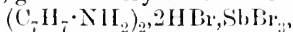
*Dihydroxycrackene*,  $C_{24}H_{16}(OH)_2$ , formed by the action of aqueous sodium hydroxide on dinitrocrackene, is a brown, amorphous mass. The constitution of crackene has not yet been determined; it is probably identical with the hydrocarbon,  $(C_4H_3)_x$ , obtained by Divers

and Nakamura from Japanese petroleum (Trans., 1885, 924), and with Schmidt and Schultz's benzerythrene (Abstr., 1878, 323; 1881, 435).  
R. H. P.

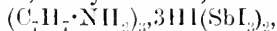
**Double Halogen Salts of Antimony with Aniline and the Toluidines.** By HOWARD H. HIGBEE (*Amer. Chem. J.*, 1900, 23, 150—173).—*Trianiline antimoniochloride*,  $(\text{NH}_2\text{Ph})_3, 3\text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$ , forms thick, colourless, monoclinic prisms, which, on exposure to the air, become opaque, and of a greenish colour; on gently heating, it decomposes, with loss of hydrogen chloride. *Aniline antimoniochloride*,  $\text{NH}_2\text{Ph}, \text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$ , forms long, thin, colourless plates. The corresponding bromides could not be obtained; *dianiline antimonio-bromide*,  $(\text{NH}_2\text{Ph})_2, 2\text{HBr}, \text{SbBr}_3$ , forms canary-yellow, lath-shaped, orthorhombic crystals, which are stable in the air; *tetraniline antimonio-bromide*,  $(\text{NH}_2\text{Ph})_4, 4\text{HBr}, \text{SbBr}_3 + \text{H}_2\text{O}$ , forms transparent, tabular, light yellow, orthorhombic crystals with a perfect cleavage, which, on keeping, become opaque. Of the *aniline antimonioiodides* (1),  $\text{NH}_2\text{Ph}, \text{HI}, \text{SbI}_3$ , crystallises in stable, minute, scarlet octahedra; (2),  $(\text{NH}_2\text{Ph})_3, 3\text{HI}, (\text{SbI}_3)_2$ , forms slender, carmine needles, whilst (3),  $(\text{NH}_2\text{Ph})_4, 4\text{HI}, \text{SbI}_3$ , separates in golden-yellow plates, which, on draining, become orange-red.

From *o*-toluidine only one *chloride*,  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_2, 2\text{HCl}, \text{SbCl}_3$ , can be obtained; the *bromide*,  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HBr}, \text{SbBr}_3$ , forms light yellow, stunted prisms. Of the *iodides*, (1),  $\text{C}_7\text{H}_7\cdot\text{NH}_2, \text{HI}, \text{SbI}_3$ , crystallises in short, brick-red needles; (2),  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HI}, (\text{SbI}_3)_2$ , forms irregular, bronze-coloured leaflets.

***m*-Toluidine Salts.**—*Chlorides*: (1),  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HCl}, \text{SbCl}_3$ , crystallises in thin, colourless, orthorhombic tables; (2),  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_2, 2\text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$ , forms colourless, granular crystals. The *bromide*,

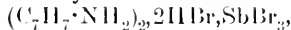


forms long, pale yellow, silky needles; the *iodide*,



lustrous, brick-red prisms.

***p*-Toluidine Salts.**—*Chlorides*: (1),  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_2, 2\text{HCl}, \text{SbCl}_3 + \frac{1}{2}\text{H}_2\text{O}$ , forms long, colourless, silky needles; (2),  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$ , colourless, granular crystals. *Bromides*: (1),



anhydrous, and also with  $\text{H}_2\text{O}$ ; (2),  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HBr}, \text{SbBr}_3$ ; (3),  $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_4, 4\text{HBr}, \text{SbBr}_3$ . In dry air, these compounds are canary-yellow, but when exposed to a damp atmosphere they become snow-white. The *iodide*,  $\text{C}_7\text{H}_7\cdot\text{NH}_2, \text{HI}, \text{SbI}_3$ , forms light orange, blunt, prismatic crystals, and darker orange-coloured needles. W. A. D.

**Action of Formaldehyde on Anilides.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1900, 24, 97).—When formanilide is dissolved in formaldehyde solution (40 per cent.) and water added, an unstable oil is precipitated which yields a sodium salt; but if the solution is left for 24 hours in the presence of hydrochloric or sulphuric acid, and then treated with sodium hydroxide, a white, amorphous base, *anhydro-p-formaminobenzyl alcohol*,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ , separates, which is easily

soluble in chloroform, yields salts, and combines with benzoyl chloride.

Formyl-*o*-anisidine yields a similar compound.

E. G.

$\psi$ -Carbamides. By ERNST MENNE (*Ber.*, 1900, 33, 657—665. Compare Gabriel, *Abstr.*, 1889, 848, &c.).—When a benzene solution of bromoethylamine, prepared by shaking the hydrobromide with 33 per cent. potassium hydroxide solution, is mixed with phenylcarbimide, *phenylbromoethylcarbamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \text{Br}$ , melting at  $106-107^\circ$ , is formed; when this is boiled with water, it is transformed into the hydrobromide of *N*-phenylethylene- $\psi$ -carbamide,

$\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{N} \cdot \text{CH}_2 \end{smallmatrix}$  (Gabriel, *Abstr.*, 1896, i, 121), the *picrate* of which

melts and decomposes at  $175^\circ$ . When phenylthiocarbimide is used instead of phenylcarbimide, the hydrobromide of the phenylethylene- $\psi$ -thiocarbamide is obtained at once, no intermediate product being formed; at the same time, a compound of the  $\psi$ -thiocarbamide with phenylthiocarbimide,  $\text{NHPh} \cdot \text{CS} \cdot \text{NPh} \cdot \text{C} \begin{smallmatrix} \text{S} \cdot \text{CH}_2 \\ \text{N} \cdot \text{CH}_2 \end{smallmatrix}$ , melting at  $113^\circ$ , is formed. The *picrate*, *aurichloride*, and *platinichloride* of the  $\psi$ -thiocarbamide melt at  $198-202^\circ$ ,  $140-142^\circ$ , and  $199-202^\circ$  respectively; by treating it with methyl iodide, the *hydriodide* of *phenylmethylethylene-ψ-thiocarbamide*, melting at  $165^\circ$ , is obtained; the corresponding base was only obtained as an oil.

By mixing aromatic bases,  $\text{NH}_2\text{R}$ , with allylcarbimide in benzene solution, allylcarbamides,  $\text{NHR} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$ , are obtained; when these are heated at  $100^\circ$  with fuming hydrochloric acid,  $\beta$ -chloropropylcarbamides,  $\text{NHR} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CHMeCl}$ , are formed, and, with

alkalis, can be converted into  $\psi$ -carbamides,  $\text{NHR} \cdot \text{C} \begin{smallmatrix} \text{O} \cdot \text{CHMe} \\ \text{N} \cdot \text{CH}_2 \end{smallmatrix}$ . The compounds obtained and analysed are enumerated below, with their melting points: *phenylallylcarbamide*,  $115.5^\circ$ ; *phenyl-β-chloropropylcarbamide*,  $121^\circ$ ; *N-phenylpropylene-ψ-carbamide*,  $132^\circ$ , *picrate*,  $166-168^\circ$ , *aurichloride*,  $168^\circ$ , *platinichloride* [ $\text{R} = \text{Ph}$ ]. Starting with methylaniline instead of aniline, *phenylmethylpropylene-ψ-carbamide* is obtained as an oil, *picrate*,  $156-157^\circ$ . *o-Tolylallylcarbamide*,  $152^\circ$ ; *o-tolyl-β-chloropropylcarbamide*,  $95-97^\circ$ ; *o-tolylpropylene-ψ-carbamide*,  $80^\circ$ , *picrate*,  $168-170^\circ$ , *aurichloride*,  $140-142^\circ$  [ $\text{R} = \text{C}_6\text{H}_4\text{Me} (o)$ ]. *m-Tolylallylcarbamide*,  $115^\circ$ ; *m-tolyl-β-chloropropylcarbamide*; *m-tolylpropylene-ψ-carbamide*,  $86-87^\circ$ , *picrate*, *aurichloride*,  $115^\circ$ , *platinichloride*,  $157^\circ$  [ $\text{R} = \text{C}_6\text{H}_4\text{Me} (m)$ ]. *p-Tolylallylcarbamide*,  $139^\circ$ ; *p-tolyl-β-chloropropylcarbamide*,  $138^\circ$ ; *p-tolylpropylene-ψ-carbamide*,  $118^\circ$ , *picrate*,  $184^\circ$ , *aurichloride*,  $167-168^\circ$ , *platinichloride*,  $185^\circ$  [ $\text{R} = \text{C}_6\text{H}_4\text{Me} (p)$ ]. *a-m-Xylallylcarbamide*,  $165^\circ$ ; *a-m-xyl-β-chloropropylcarbamide*; *a-m-xylpropylene-ψ-carbamide*,  $86-88^\circ$ , *picrate*,  $172-174^\circ$ , *aurichloride*, *platinichloride*, [ $\text{R} = \text{C}_6\text{H}_3\text{Me}_2 (2:4)$ ]. *o-Anisylallylcarbamide*,  $112^\circ$ ; *o-anisyl-β-chloropropylcarbamide*,  $103^\circ$ ; *o-anisylpropylene-ψ-carbamide*,  $87-88^\circ$ , *aurichloride*,  $129^\circ$ , *platinichloride*,  $160-161^\circ$  [ $\text{R} = \text{C}_6\text{H}_4 \cdot \text{OMe} (o)$ ]. *m-Phenetylallylcarbamide*,  $154^\circ$ ; *m-phenetyl-β-chloropropylcarbamide*,  $116^\circ$ ; *m-phenetylpropylene-ψ-carbamide*,  $112-113^\circ$ , *picrate*,  $166-168^\circ$ , *aurichloride*,  $150^\circ$ , *platinichloride*,  $180^\circ$  [ $\text{R} = \text{C}_6\text{H}_4 \cdot \text{OEt} (m)$ ]. C. F. B.

**Action of Phenylcarbimide on Ethyl  $\beta$ -Aminocrotonate.** By ROBERT BEHREND and FERD. C. MEYER (*Ber.*, 1900, **33**, 621—624).—Two compounds are formed by the action of phenylcarbimide on ethyl  $\beta$ -aminocrotonate.

1. *Ethyl  $\beta$ -phenyluraminocrotonate*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , which is readily soluble in ether, but crystallises from light petroleum in broad, glistening needles melting at  $98-99^\circ$ . Its constitution follows from the fact that, on hydrolysis with alcoholic potash, it yields phenylmethylylacil.

2. An isomeric compound,  $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}\cdot\text{NHPh})\cdot\text{CO}_2\text{Et}$ , which is almost insoluble in ether; it crystallises from boiling alcohol in needles melting at  $125-126^\circ$ ; on hydrolysis with alcoholic potash, it yields ammonia, carbon dioxide, aniline, and a compound melting at  $83-84^\circ$ , probably acetoacetanilide, and on treatment with concentrated sulphuric acid it yields ethyl acetylmalanilate (*Abstr.*, 1896, i, 593).

Phenylthiocarbimide and ethyl  $\beta$ -aminocrotonate yield a thick oil, together with crystals of *ethyl thiouraminocrotonate*, melting at  $135^\circ$ , which on hydrolysis yields *phenylthiomethylylacil*, melting at  $255^\circ$ . Methylthiocarbimide gives a product melting at  $146-147^\circ$ .

In a note BEHREND states that the two dimethyluracils (this vol., i, 120) are structurally isomeric, although they yield the same oxaluric acid, and he now agrees with Fischer's conclusion that  $\delta$ -methyluric acid is 4-methyluric acid, not 6-methyluric as he formerly held (*Behrend and Dietrich*, this vol., i, 120). J. J. S.

**Vinylideneoxanilide and its Homologues.** By HANS VON PECHMANN and OTTO ANSEL (*Ber.*, 1900, **33**, 613—621. Compare

*Abstr.*, 1897, i, 135, 187).—The constitution,  $\begin{matrix} \text{CO}\cdot\text{NPh} \\ | \\ \text{CO}\cdot\text{NPh} \end{matrix} > \text{C}\cdot\text{CH}_2$ , assigned to vinylideneoxanilide is supported by the fact that only those fatty acids which contain at least one hydrogen atom attached to the  $\alpha$ -carbon atom are capable of yielding similar derivatives with oxanilide. Vinylideneoxanilide is capable of undergoing two separate decompositions—an *anilide* decomposition into acetic acid and oxanilide or oxanilic acid and aniline, and an *amidine* decomposition into oxalic acid and vinylidenediphenyldiamine, which then becomes transformed into ethenyldiphenylamidino. The former hydrolysis is most readily brought about by the aid of alcoholic solutions of acids, or by ammonia and aniline; the latter hydrolysis by alcoholic potassium hydroxide, but the two may occur simultaneously. Vinylideneoxanilide is formed when the three dicarboxylic derivatives of oxanilide are heated with acetic anhydride and sodium acetate. Bromoethenyldiphenylamidino (*loc. cit.*) melts at  $159^\circ$  and not at  $189^\circ$ . *Ethylidene-*

*oxanilide*,  $\begin{matrix} \text{CO}\cdot\text{NPh} \\ | \\ \text{CO}\cdot\text{NPh} \end{matrix} > \text{CHMe}$ , formed when the vinylidene compound is reduced with zinc dust and alcohol in the presence of a little calcium chloride, crystallises from alcohol in glistening plates melting at  $218-219^\circ$ , and is readily soluble in most organic solvents; when warmed with alcoholic potash, it yields oxalic acid and Eibner's ethyldenediphenyldiamine. *Methyl oxanilide-m-dicarboxylate*, obtained by

heating methyl *m*-aminobenzoate and oxalic acid over the free flame, forms a crystalline powder melting at  $236^{\circ}$ , and when heated for 6—7 hours with sodium acetate and acetic anhydride, yields *methyl vinylidenexanilide-m-dicarboxylate*, which crystallises in glistening needles melting at  $194^{\circ}$  and is sparingly soluble in alcohol or benzene.

Glyoxime-*N*-*p*-tolyl ether, sodium acetate, and acetic anhydride yield *vinylidene-p-oxalotoluidide*,  $\begin{matrix} \text{CO}\cdot\text{N}(\text{C}_7\text{H}_7) \\ | \\ \text{CO}\cdot\text{N}(\text{C}_7\text{H}_7) \end{matrix} > \text{C}:\text{CH}_2$ , which crystallises

from alcohol in glistening scales melting at  $178^{\circ}$ ; when warmed with alcoholic potash, it yields *p*-ditolylethenylamidine melting at  $121$ — $121.5^{\circ}$ , and, when reduced, *ethylidene-p-oxalotoluidide*, crystallising in long, glistening plates melting at  $223^{\circ}$ ; when this is treated with alcoholic potash, it yields *ethylidene-p-ditolylidiamine*,  $\text{CHMe}(\text{NH}\cdot\text{C}_7\text{H}_7)_2$ , melting at  $61^{\circ}$ .

*Bromovinylidene-β-oxalotoluidide*,  $\text{C}_3\text{N}_2\text{O}_2(\text{C}_7\text{H}_7)_2\cdot\text{CHBr}$ , obtained by the action of bromine on a chloroform solution of vinylidenexanilide, crystallises from alcohol in prisms which turn brown at  $140^{\circ}$  and melt at  $160^{\circ}$ ; on treatment with alcoholic potash, it is converted into *p-ditolylbromoethenylamidine*,  $\text{C}_7\text{H}_7\cdot\text{N}:\text{C}(\text{CH}_2\text{Br})\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , which crystallises in glistening plates melting at  $148^{\circ}$ .

Glyoxime-*N*-1 : 3 : 4-xylyl ether, sodium acetate, and acetic anhydride yield an *oxalylo-xylylidide* melting at  $205^{\circ}$ .

*Methylvinylidenexanilide*,  $\begin{matrix} \text{CO}\cdot\text{NPh} \\ | \\ \text{CO}\cdot\text{NPh} \end{matrix} > \text{C}:\text{CHMe}$ , obtained from oxanilide, sodium propionate, and propionic anhydride, or, still better, from glyoxime-*N*-phenyl ether, separates from its hot chloroform solution, on the addition of light petroleum, as small prisms melting at  $274$ — $275^{\circ}$ ; on treatment with alcoholic potash, it yields diphenylpropenylamidine.

*Dimethylvinylidenexanilide*, obtained from sodium isobutyrate, isobutyric anhydride, and oxanilide, forms glistening needles melting at  $196$ — $198^{\circ}$ , and readily soluble in hot alcohol or chloroform. *Diphenylisobutenylamidine*,  $\text{NPh}:\text{CPr}^{\beta}\cdot\text{NHPh}$ , crystallises in transparent prisms melting at  $90$ — $91^{\circ}$ .

*Dimethylethylacetic* [*α*-*dimethylbutyric*] *anhydride* is a colourless liquid distilling at  $227$ — $228^{\circ}$ , and does not react with oxanilide or glyoxime-*N*-phenyl ether. J. J. S.

**4 : 1-Chloronaphthylamine.** By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1900, 33, 682—684).—The principal product of the chlorination of 1-acetylaminonaphthalene (compare Cleve, *Abstr.*, 1887, 494) by sodium acetate and hydrochloric acid in acetic acid solution is 4 : 1-chloroacetylaminonaphthalene (m. p.  $186.5^{\circ}$ ), which on hydrolysis yields 4 : 1-chloronaphthylamine melting at  $98^{\circ}$ ; the latter is identical with Seidler's chloro-*α*-naphthylamine of undetermined constitution (*Abstr.*, 1878, 983), whilst Atterberg's 4 : 1-chloronaphthylamine, (*Ber.*, 1877, 10, 547) melting at  $85$ — $86^{\circ}$ , is impure and after recrystallisation from light petroleum melts at  $98^{\circ}$ . W. A. D.

**Constitution of Tribromophenol Bromide** ("Tribromophenol-brom"). By JOHANNES THIELE and HEINRICH EICHWEDE (*Ber.*, 1900, 33, 673—674).—Tribromophenol bromide is converted by lead acetate

at 60—70° in dilute acetic acid solution into 2:6-dibromoquinone. It must therefore have the formula  $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CH} \\ \text{CBr}:\text{CH} \end{smallmatrix} \text{CBr}_2$ . Yet it does not form a semicarbazone; instead, it oxidises the semicarbazide, becoming itself reduced to tribromophenol. C. F. B.

**Anethole and its Isomerides.** By WILLIAM R. ORNDORFF and D. A. MORTON (*Amer. Chem. J.*, 1900, 23, 181—202. Compare Abstr., 1898, i, 129).—From the authors' previous work (*loc. cit.*), it seemed probable that anethole and liquid metanethole are stereoisomerides bearing the same relation to one another as fumaric and maleic acids. By a careful examination of their physical and chemical properties, and also of those of their derivatives, these two compounds are now shown to be identical.

By the action of alcoholic potash on anethole, an additive compound,  $\text{C}_{10}\text{H}_{12}\text{O}, \text{C}_2\text{H}_6\text{O}$ , is formed as a thin, colourless oil, lighter than water; it has a pleasant, mint-like odour, does not decolorise bromine, and when heated decomposes into anethole, alcohol, and solid metanethole.

**Anethole hydrobromide**,  $\text{C}_{10}\text{H}_{12}\text{O}, \text{HBr}$ , is a heavy oil resembling the hydrochloride.

On distilling anisoin, it decomposes into anethole and isoanethole, together with a small proportion of *p*-methoxytoluene.

An improved method for the preparation of anisoin is given.

T. H. P.

**Action of Picryl Chloride on Catechol in Presence of Alkalis.** By HOMER W. HILLYER (*Amer. Chem. J.*, 1900, 23, 125—128).—On warming a mixture of picryl chloride (1 mol.) and catechol (1 mol.) dissolved in alcohol containing sodium (2 at.) for 6 hours at 60—70°, sodium chloride and nitrite are formed, together with 3:5-dinitro-*o*-diphenylene oxide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_2$ ; to indicate the analogy of this substance with dinitrophenoxazino (Turpin, *Trans.*, 1891, 69, 714), the name *dinitrophenoxozone* is proposed. It crystallises from glacial acetic acid in lemon-yellow, spherical aggregates, melts at 192—192.5°, and decomposes when rapidly heated, but sublimes in yellow leaflets when cautiously heated; it is indifferent towards dilute alkalis and hydrochloric acid, and dissolves unchanged in concentrated sulphuric acid, being precipitated on dilution.

W. A. D.

**Preparation of Resorcinol Monomethyl Ether.** By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1900, [ii], 61, 109—113).—In preparing resorcinol monomethyl ether by heating resorcinol with potassium hydrogen sulphate and methyl alcohol (Wallach and Wüsten, *Abstr.*, 1883, 1096), the yield amounted in three experiments to 30, 33, and 35 per cent. of the theoretical.

T. M. L.

**Eugenol, Safrole, and Propylcatechol.** By RAYMOND DELANGH (*Compt. rend.*, 1900, 130, 659—660).—**Propylcatechol**,  $\text{C}_6\text{H}_3\text{Pr}(\text{OH})_2$  [ $\text{Pr}:\text{OH}:\text{OH}=1:3:4$ ], is obtained (1) by methylating eugenol, boiling the resulting allylveratrole with alcoholic potash to convert it into the

isomeric propenylveratrole, reducing the latter by means of sodium and boiling alcohol, and treating the propylveratrole thus obtained with hydriodic acid; (2) by boiling safrole with alcoholic potash, reducing the isosafrole thus formed to propylmethylenecatechol, treating the latter with phosphorus pentachloride, and decomposing the dichloride produced with water. Propylcatechol is a white, crystalline compound of faint, agreeable odour; it melts at  $60^{\circ}$ , boils at  $175-180^{\circ}$  under 30 mm. pressure, and is slightly soluble in water and very soluble in most organic solvents. The aqueous solution reduces ammoniacal silver nitrate in the cold, and yields a greenish-blue coloration with ferric chloride, which is changed to wine-red by the addition of sodium carbonate.

N. L.

**Nitroso-derivatives of the Phloroglucinol Ethers.** By HUGO WEIDEL and JACQUES POLLAK (*Monatsh.*, 1900, **21**, 15—35. Compare Abstr., 1898, i, 15).—*Phloroglucinol monomethyl ether*, prepared by the etherification of phloroglucinol at low temperatures, boils at  $213^{\circ}$  under 16 mm. pressure, and solidifies to a yellowish mass of crystals, which melts at  $75-78^{\circ}$ ; by the authors' method of treatment (*loc. cit.*), it yields a diisonitroso-derivative, probably  $\text{OMe} \begin{smallmatrix} \text{C}(\text{N}\cdot\text{OH})\cdot\text{CO} \\ \text{CH} \text{---} \text{CO} \end{smallmatrix} \text{C}:\text{N}\cdot\text{OH}$ , which forms a reddish-yellow mass of crystals melting at about  $150^{\circ}$ , gives a characteristic monopotassium derivative, and on reduction with stannous chloride and hydrochloric acid, yields 2:4-diamino-3:5-dihydroxyanisole hydrochloride, which decomposes on exposure to the air, but forms a well-characterised tetra-acetyl derivative melting at  $169^{\circ}$ .

When phloroglucinol dimethyl ether is treated with a nitrite and acetic acid, the greater part is converted into 3:5-dimethoxy-o quinone-2-monoxime, small quantities of 3:5-dimethoxy-p-quinone-2-monoxime being formed at the same time. 3:5-Dimethoxy-o-quinone-2-monoxime crystallises from alcohol in dark red, lustrous leaflets melting at  $175-176^{\circ}$ , and on reduction with stannous chloride and hydrochloric acid yields 2-amino-3:5-dimethoxyphenol hydrochloride, which forms reddish needles melting at  $205-206^{\circ}$ , and on fusion with carbamide, yields 3:5-dimethoxycarbonyl-2-aminophenol,  $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{C}\cdot\text{C}(\text{OMe})\cdot\text{CH} \\ \text{O} \text{---} \text{C} \text{---} \text{CH}=\text{C}\cdot\text{OEt} \end{smallmatrix}$ , which crystallises in needles melting at  $210-211^{\circ}$ .

3:5-Dimethoxy-p-quinone-4-monoxime forms long, yellow needles, which become coloured at  $185^{\circ}$  and melt at  $222^{\circ}$ ; on reduction, it yields 4-amino-3:5-dimethoxyphenol hydrochloride, which crystallises from dilute hydrochloric acid, with  $\text{H}_2\text{O}$ , in snow-white, silky needles melting and decomposing at  $171-173^{\circ}$ , and is oxidised by ferric chloride to 3:5-dimethoxyquinone, thus affording a proof of the constitution of the p-quinonemonoxime. The 4-amino-3:5-diethoxyphenol hydrochloride previously described (*loc. cit.*) yields, on treatment with ferric chloride, an analogous 3:5-diethoxyquinone, which crystallises from chloroform in yellow needles melting at  $118-122^{\circ}$ , and gives a characteristic red coloration with concentrated sulphuric acid.

R. H. P.

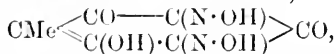


**Ethylphloroglucinol and other Derivatives of Ethylbenzene.** By GUSTAV WEISWEILLER (*Monatsh.*, 1900, 21, 39—49).—2 : 4-Dinitro-1-ethylbenzene, prepared by the action, at 125—130°, of a mixture of 1 part of nitric acid, of sp. gr. 1.43, and 2 parts of sulphuric acid on ethylbenzene, is a viscous, yellow oil which boils at 167.5° under 13 mm. pressure; when reduced by tin and hydrochloric acid, it yields 2 : 4-diamino-1-ethylbenzene dihydrochloride, which is colourless when crystallised from alcohol, but becomes dark red on contact with water; the diacetyl derivative of the corresponding base is formed when the dihydrochloride is treated with acetic anhydride, and crystallises in slender needles melting at 224°; the monoacetyl derivative formed in small quantities at the same time melts at 319—320°.

*s*-Trinitroethylbenzene is prepared by the action of a mixture of 1 part of nitric acid, of sp. gr. 1.525, and 4 parts of fuming sulphuric acid ( $\text{SO}_3 : 2\text{H}_2\text{SO}_4$ ) on ethylbenzene; it is separated from the dinitro-derivative by means of the additive compound with aniline,  $\text{C}_6\text{H}_5\text{Et}(\text{NO}_2)_3 + \text{NH}_2\text{Ph}$ , which is precipitated by light petroleum from a benzene solution of aniline and the crude nitration product in red needles melting at 44—45°. This additive compound is decomposed by acids into an aniline salt and *s*-trinitroethylbenzene, which crystallises from alcohol in yellow leaflets melting at 37°; on reduction with tin and hydrochloric acid, it yields diaminohydroxyethylbenzene dihydrochloride, which yields a triacetyl derivative of the base, forming small, white needles melting at 259—262°. When the dihydrochloride is treated with a large excess of water, it is converted into ethylphloroglucinol,  $\text{C}_6\text{H}_2\text{Et}(\text{OH})_3$ , which boils at 209—210° under 12 mm. pressure, and solidifies to a mass of white crystals melting at 119—120°; it yields a liquid triacetyl derivative, which boils at 208—209° under 15.8 mm. pressure.

R. H. P.

**Action of Nitrous Acid on Methylphloroglucinol.** By HUGO WEIDEL and JACQUES POLLAK (*Monatsh.*, 1900, 21, 50—61. Compare preceding page).—Methylphloroglucinol, on treatment with a nitrite and acetic acid, yields a diisonitroso-derivative,



which crystallises from water, with  $\text{H}_2\text{O}$ , in bright, yellow needles melting at 154—155°, and forms a characteristic copper-red potassium salt; on reduction, this gives the very unstable 3 : 5-diamino-2 : 4 : 6-trihydroxytoluene hydrochloride, which is characterised by the penta-acetyl derivative, crystallising in needles and melting at 217—218°. During the preparation of this acetyl derivative, a compound of undetermined composition is obtained, which forms lustrous tablets melting at 114°. When the diisonitroso-compound is treated with hydroxylamine and alcohol, a monoxime is obtained, which melts at 189—190°, and, on reduction with tin and hydrochloric acid, yields a triaminodihydroxytoluene dihydrochloride. The constitutions of this oxime and of its reduction product have not yet been determined.

R. H. P.

**Preparation of Dimethyl-1 : 2 : 3 : 5 phentetrol.** By HEINRICH BRUNNMAYER (*Monatsh.*, 1900, 21, 1—14).—Nitrosodimethylphloroglucinol is easily obtained by treating dimethylphloroglucinol at -5°

with nitric acid, which has been saturated with nitrous acid; it crystallises in orange-red tablets melting at  $158^{\circ}$ , and colours concentrated hydrochloric acid an intense violet, but does not give Liebermann's reaction; it is easily reduced by stannous chloride, yielding *amino-dimethylphloroglucinol hydrochloride*, which crystallises with  $H_2O$  in colourless needles, and on treatment with acetic anhydride yields a *penta-acetyl* derivative, which crystallises in small, lustrous cubes melting at  $169^{\circ}$ . *Dihydroxy-m-xyloquinone*, obtained by the oxidation of the hydrochloride just mentioned with ferric chloride, crystallises in deep red, lustrous leaflets, which melt and sublime at  $167^{\circ}$ ; it is strongly acidic, dissolving in alkaline liquids giving a deep blue-violet coloration. On reduction by stannous chloride in acid solution, it yields *dimethyl-1:2:3:5-phentetrol*, which crystallises from light petroleum in pale rose-coloured needles melting at  $189^{\circ}$ , gives similar colour reactions to those described by Oettinger (Abstr., 1895, i, 457) for 1:2:3:5-phentetrol, and yields a *tetra-acetyl* derivative which crystallises in colourless, transparent needles melting at  $154^{\circ}$ . R. H. P.

**$\psi$ -Phenylacetic Acid.** By WILHELM BRAREN and EDUARD BUCHNER (Ber., 1900, 33, 684—691. Compare Abstr., 1898, i, 639—640).—On reducing bromocycloheptenecarboxylic acid (*loc. cit.*) with zinc dust and acetic acid,  $\Delta^1$ -cycloheptenecarboxylic acid (suberenecarboxylic acid), melting at  $51$ — $52^{\circ}$ , is formed, together apparently with a smaller proportion of the isomeric  $\Delta^2$ -acid, although the latter could not be isolated.  $\beta$ -Isophenylacetic acid, on reduction with sodium amalgam at the ordinary temperature, gives rise to  $\Delta^2$ -cycloheptenecarboxylic acid, which melts at  $18$ — $20^{\circ}$ , boils at  $250$ — $253^{\circ}$  under 735 mm. pressure, and is identical with the so-called  $\Gamma\alpha$ - $\Delta^2$ -1:4-ethylcyclopentenecarboxylic acid obtained by Einhorn and Willstätter (Abstr., 1894, i, 523) on reducing *p*-methylenedihydrobenzoic acid (Abstr., 1893, i, 378); the amides of both acids are also identical. When  $\Delta^2$ -cycloheptenecarboxylic acid is heated with alcoholic potassium hydroxide, it undergoes rearrangement into the foregoing  $\Delta^1$ -acid.

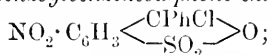
Bromocycloheptenecarboxylic acid readily unites with bromine at the ordinary temperature in glacial acetic acid solution to form *tribromocycloheptenecarboxylic acid*, which crystallises from formic acid, melts at  $161$ — $162^{\circ}$ , and is stable towards aqueous potassium permanganate.

In a supplementary note, E. BUCHNER deals very fully with Willstätter's contention (Abstr., 1899, i, 651) that the amide of  $\Delta^1$ -cycloheptenecarboxylic acid melts at  $134$ — $135^{\circ}$ ; it is maintained that the true melting point is  $126^{\circ}$ . W. A. D.

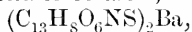
**Symmetrical *p*-Nitro-*o*-sulphobenzoic Chloride.** By FRED S. HOLLIS (Amer. Chem. J., 1900, 23, 233—255).—By heating potassium hydrogen *p*-nitro-*o*-sulphobenzoate (1 mol.) with phosphorus pentachloride (2.5 mols.) at  $150^{\circ}$  for 5 hours, the unsymmetrical dichloride of the acid is alone formed (compare Remsen and Gray, Abstr., 1897, i, 477).

The action of benzene and aluminium chloride on either the sym-

metrical or the unsymmetrical dichloride of *p*-nitro-*o*-sulphobenzoic acid gives rise to *p*-nitro-*o*-benzoylbenzenesulphonic chloride,



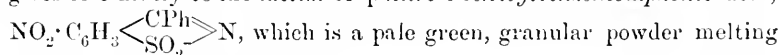
it separates from benzene on adding ether in the form of small, purple, or green, apparently monoclinic crystals, having a rhombohedral habit, and melts at 177°. By the action of either hydrochloric acid, sulphuric acid, water, or alcohol on the sulphonic chloride, *p*-nitro-*o*-benzoylbenzenesulphonic acid is formed; its *barium* salt,



forms monoclinic crystals containing varying amounts of water of crystallisation and has an intensely bitter taste; the *sodium* (with  $\text{H}_2\text{O}$ ), *potassium*, *magnesium* (with  $9\frac{1}{2}\text{H}_2\text{O}$ ), *calcium* (with  $3\text{H}_2\text{O}$ ), and *lead* (with  $5\frac{1}{2}\text{H}_2\text{O}$ ) salts are described.

On heating phosphorus pentachloride and sodium *p*-nitro-*o*-benzoylbenzenesulphonate together, the corresponding sulphonic chloride, just described, is obtained.

The action of ammonia on *p*-nitro-*o*-benzoylbenzenesulphonic chloride gives rise firstly to the *lactim* of *p*-nitro-*o*-benzoylbenzenesulphonic acid,



at 234°; it dissolves readily in benzene, but only slightly in alcohol, and by the continued action of ammonia suffers decomposition. Concentrated hydrochloric acid at a high temperature converts the lactim into *ammonium p*-nitro-*o*-benzoylbenzenesulphonate, which forms either a yellow, crystalline powder or thick, acicular crystals; it dissolves readily in water and gives no definite melting point. T. H. P.

**Rearrangement of Imino-ethers. II.** By HENRY L. WHEELER (*Amer. Chem. J.*, 1900, 23, 135—150. Compare Wheeler and Johnson, *Abstr.*, 1899, i, 431).—Methyl iodide acts on benziminomethyl ether at the ordinary temperature in the same manner as at 100°, benzomethylamide being formed along with benzamide, benzonitrile, and a trace of cyanphenin; the proportion of methyl iodide used has no influence on the result. Similar results were obtained with ethyl iodide and benziminoethyl ether (compare *loc. cit.*); in this action, no benzodiethylamide is formed. On heating benziminoisobutyl ether with methyl iodide for 4 hours at 80—115°, isobutyl iodide and benzomethylamide are formed, together with a smaller proportion of benzamide and cyanphenin; benzomethylamide melts at 82°, not at 78° as stated by Romburgh (*Rec. Trav. Chim.*, 1886, 4, 387). When benziminoisobutyl ether is heated at 165—185° for several hours with isobutyl iodide, the latter is decomposed into isobutylene and hydrogen iodide, which converts the imino-ether into benzamide with regeneration of isobutyl iodide; *benzoisobutylamide*, prepared from isobutylamine by the Baumann-Schotten reaction, crystallises from alcohol in chisel-shaped prisms, melts at 57—58°, and boils at 173—178° under 13 mm. pressure, and with partial decomposition at 308—313° under 760 mm. pressure. Benziminoethyl ether and isobutyl iodide yield benzamide, benzonitrile, cyanphenin, benzethylamide, benzoisobutyl-

amide, and a small quantity of a *substance* separating from alcohol in colourless crystals and melting with effervescence at 192°.

[With TREAT B. JOHNSON.]—Phenylacetiminomethyl ether and methyl iodide, when heated together at 95—105°, yield phenylacetamide, phenylacetomitrile, and phenylacetomethylamide; quantitative experiments show that neither the amount of methyl iodide used nor the time of heating influences the relative proportions of the products formed. Phenylacetiminoethyl ether and ethyl iodide in a similar manner give phenylacetoethylamide.

[With MUNSON D. ATWATER.]—*Furfuriminomethyl ether*,  
 $\text{OMe} \cdot \text{C}(\text{C}_4\text{OH}_3) \cdot \text{NH}$ ,

prepared from furfuryl cyanide by Pinner's method, is a colourless oil with a characteristic odour which boils at 52—57° under 8 mm. and at 169—172° under 762 mm. pressure; with methyl iodide, either at the ordinary temperature or at 100°, it yields a small quantity of pyromucamide, together with a larger proportion of *pyromucomethylamide*,  $\text{C}_6\text{H}_4\text{O}_2\text{N}$ , which crystallises from light petroleum and forms stout, colourless crystals, melts at 64°, and boils at 250—253° under the ordinary pressure.

*p-Tolonyliminomethyl ether*, prepared from *p*-toluonitrile by Pinner's method, boils at 105·5° under 10·5 mm. pressure; with methyl iodide, it yields *p*-toluomethylamide [m. p. 144—145°; Gattermann and Schmidt (*Annalen*, 1887, 244, 51) give 143°]. When heated with methyl alcohol at 100—140° for 6 hours and finally at 150—175°, it yields *p*-toluonitrile and a small quantity of *p*-toluamide, no molecular rearrangement occurring.

*β-Naphthyliminoethyl ether*, prepared from *β*-naphthonitrile, when heated with ethyl iodide, yields only a small proportion of *β*-naphthoethylamide (m. p. 129—131°).

[With BAYARD BARNES.]—Although silver succinimide yields oxygen-ethers with alkyl iodides at the ordinary temperature (Comstock and Wheeler, *Abstr.*, 1892, 701), nitrogen-ethers are obtained at higher temperatures owing to rearrangement occurring; methyl iodide at 100° yields succinomethylimide, and ethyl iodide during 12 hours at 100°, succinoethylimide, together with a certain proportion of the oxygen-ether, characterised by the compound it forms with aniline (*loc. cit.*).

Benzoylbenziminioethyl ether,  $\text{OEt} \cdot \text{CPh} \cdot \text{NBz}$ , when heated with ethyl iodide for 8 hours at 110—120°, does not undergo rearrangement, but is decomposed into benzonitrile and ethyl benzoate.

W. A. D.

Decomposition of Benzenylmethyliminochloride. By HANS VON PECHMANN [with JULIUS OBERMILLER] (*Ber.*, 1900, 33, 611—612. Compare *Abstr.*, 1896, i, 31).—The compound previously obtained by distilling benzenylmethyliminochloride under diminished pressure is now shown to be cyanphenin. When the same iminochloride is boiled for some time, or is distilled several times, under atmospheric pressure, it is decomposed into methyl chloride and benzonitrile.

From Wallach's researches, it follows that aromatic substituted

iminochlorides of aromatic acids can be distilled without undergoing decomposition, whereas aromatic and aliphatic derivatives of iminochlorides of aliphatic acids are readily decomposed. The authors think it probable that aliphatic substituted iminochlorides of aromatic acids are readily decomposed into alkyl chlorides and aromatic nitriles or their polymerides.

J. J. S.

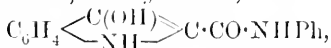
**Isomeric Mono-esters of Phenylglycine-*o*-carboxylic Acid.** By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Ber.*, 1900, 33, 553—554).—Mono-esters of phenylglycinecarboxylic acid of the constitution  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$  are obtained by the direct esterification of the acid, or by heating anthranilic acid with the esters of monochloroacetic acid. The *methyl* ester melts at  $160^\circ$ , and the *ethyl* ester at  $152^\circ$ . The isomeric mono-esters are obtained by the partial hydrolysis of the di-esters. Both the *methyl* and *ethyl* esters melt somewhat indefinitely at about  $182^\circ$ , after first softening.

A. H.

**Action of Ammonia and Aniline on Phenylglycine-*o*-carboxylic Acid.** By DANIEL VORLÄNDER and H. WEISSERENNER (*Ber.*, 1900, 33, 555—556).—Ammonia and aniline react chiefly with the aliphatic carboxyl group of phenylglycine-*o*-carboxylic acid, or its esters. *Ethyl aminophenylglycine-*o*-carboxylate*,



crystallises in white needles melting at  $180$ — $182^\circ$ . The *diamide* forms narrow plates melting at  $198$ — $200^\circ$ . *Anilinophenylglycine-*o*-carboxylic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , crystallises in white needles and melts and decomposes at  $235^\circ$ ; the corresponding *methyl* ester melts at  $140$ — $142^\circ$ , and the *ethyl* ester at  $164$ — $166^\circ$ . When the methyl or ethyl ester of the anilino compound is treated with sodium ethoxide free from alcohol, *indoxylanilide*,



is produced; it crystallises in colourless needles, and decomposes gradually when slowly heated; when rapidly heated, indigotin is formed.

A. H.

**Acetylation of Phenylglycine-*o*-carboxylic Acid.** By DANIEL VORLÄNDER and H. WEISSERENNER (*Ber.*, 1900, 33, 556—557).—*Diethyl acetylphenylglycine-*o*-carboxylate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained by the action of acetic anhydride or acetyl chloride on diethylphenylglycine-*o*-carboxylate, crystallises in large, colourless tablets and melts at  $61^\circ$ . By sulphuric acid, containing more than 99.1 per cent. of acid, it is converted at  $100^\circ$  into indigotinsulphonic acid, whilst a weaker acid does not produce indigotin. Indigotin is also produced when the compound is boiled with 20 per cent. aqueous potash and the solution exposed to the air. Acetylphenylglycine-*o*-carboxylic acid forms white crystals, which melt and decompose at about  $210^\circ$ . This acid is identical with that prepared from acetyl-*o*-tolylglycine (German Patent 102893). It is readily converted into indigotin by strong sulphuric acid, but not by alkalis.

A. H.

**Benzenestearosulphonic [Sulphophenylstearic] Acid and other Sulphonic Acids containing the Stearyl Group.** By ERNST TWITCHELL (*J. Amer. Chem. Soc.*, 1900, 22, 22—26).—*Sulphophenylstearic acid*,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_{18}\text{H}_{35}\text{O}_2$ , is formed when a mixture of benzene and oleic acid is treated with an excess of sulphuric acid, care being taken to avoid any excessive rise in temperature. When dried at  $100^\circ$ , it forms a very viscous oil which, on cooling, sets to a semi-solid mass. The acid and both its normal and acid alkali salts are soluble in water, yielding colloidal solutions, and are precipitated by the addition of an acid, alkali, or salt. The acid is only slowly decomposed by heating at  $170^\circ$  with hydrochloric acid, and when fused with potash it gives potassium sulphite.

*Sulphonaphthylstearic Acid*,  $\text{SO}_3\text{H} \cdot \text{C}_{10}\text{H}_6 \cdot \text{C}_{18}\text{H}_{35}\text{O}_2$ , is rather less fluid than the benzene compound; *sulphophenolstearic acid* has not been obtained in a pure form. J. J. S.

**Constitution of Chrysenic Acid.** By CARL GRAEBE (*Ber.*, 1900, 33, 680—681).—In the preparation of chrysenic acid, according to Bamberger and Burgdorf's method (*Abstr.*, 1890, 1312), by fusing chrysoquinone with a caustic alkali, a better yield is obtained when lead dioxide is added. Besides the chrysenic acid melting at  $190^\circ$  (corr.), an isomeride, melting at  $114^\circ$  and more soluble, is obtained; this is named  $\beta$ -chrysenic acid. Both acids also result from the action

of caustic alkali on chrysoketone,  $\text{C}_{10}\text{H}_6 > \text{CO}$ . Of the two possible formulæ, that in which the two ortho-positions relatively to the

carboxyl are substituted,  $\text{CH}:\text{CH} \cdot \overset{\text{CH}:\text{CH}}{\underset{\text{CH}:\text{CH}}{\text{C}}} \cdot \text{CH} = \text{CH}$  must be assigned to  $\beta$ -chrysenic acid, which does not yield an ester when treated with methyl alcohol and sodium chloride at the ordinary temperature, whilst to chrysenic acid, which does form an ester, the other formula,  $\text{CH}:\text{CH}:\text{C} \cdot \text{C}_{10}\text{H}_7$  must be given. C. F. B.

**Preparation of Naphthalic Acid.** By GEORGE F. JAUBERT (*Ber.*, 1900, 33, 649).—A reply to Anselm and Zuckmayer (this vol., i, 175). T. H. P.

**3:4-Dichloro-2-dimethylaminobenzoylbenzoic Acid.** By ÉMILE SEVERIN (*Compt. rend.*, 1900, 130, 723—725).—3:4-Dichloro-2-dimethylaminobenzoylbenzoic acid,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO}_2\text{H}$ , prepared by Haller and Guyot's method (*Abstr.*, 1894, i, 602) from 3:4-dichlorophthalic anhydride and dimethylaniline, crystallises from alcohol in yellow flakes melting at  $222^\circ$ . The acetate (mixed anhydride),  $\text{NMe}_2 \cdot \text{C}_{13}\text{H}_6\text{OCl}_2 \cdot \text{CO} \cdot \text{OAc}$ , formed by heating it with acetic anhydride on the water-bath for 2 hours, crystallises from hot benzene or alcohol in colourless leaflets and melts at  $170^\circ$ .

The methyl ester of the above acid, produced by treating the preceding compound with the theoretical quantity of sodium methoxide, forms highly refractive crystals melting at  $160^\circ$ ; it cannot be obtained from its acid by the ordinary methods of esterification, the latter substance belonging to the category of ortho-disubstituted acids studied by V. Meyer.

The *ethyl* ester crystallises in colourless needles and melts at 156°.

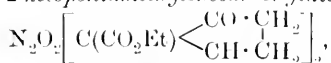
The *nitroso*-compound,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO}_2\text{H}$ , formed by the action of sodium nitrite on the acid dissolved in acetic acid, crystallises from methyl alcohol in yellow needles containing 1 mol. of the solvent, and melts at 165°.

G. T. M.

Nitroso-compounds derived from Cyclic 2-Ketocarboxylic Esters (Bisnitroso 2-ketocarboxylic Esters and  $\alpha$ -Oximinodicarboxylic Acids). By WILHELM DIECKMANN (*Ber.*, 1900, 33, 579—595).—The cyclic 2-ketocarboxylic esters, on treatment with ethyl nitrite and sodium ethoxide, yield the corresponding  $\alpha$ -oximinodicarboxylic acids, which are decomposed by heat, with formation of the half-nitrile of the next lower homologue; when, however, ethyl nitrite and hydrochloric acid or acetyl chloride are used, the 2-ketocarboxylic esters are partly converted into bisnitroso-2-ketocarboxylic esters, a class of compounds which are very similar to the bisnitroso-compounds of the terpene series (von Baeyer, *Abstr.*, 1895, i, 379), and on treatment with alcoholic potash are easily converted into the  $\alpha$ -oximinodicarboxylic acids.

*Ethyl  $\alpha$ -oximinoadipate*, obtained from ethyl 2-ketopentamethylene carboxylate, forms colourless needles melting at 52—53°, and on hydrolysis yields  *$\alpha$ -oximinoadipic acid*,  $\text{CO}_2\text{H} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ , which forms small, white crystals melting at 151—152°, yields a characteristic *silver hydrogen* salt, and when heated above its melting point decomposes with the formation of  *$\gamma$ -cyanobutyric acid*, which crystallises in very hygroscopic, colourless tablets melting at about 45°.

*Diethyl bisnitroso-2-ketopentamethylenecarboxylate*,



obtained from ethyl 2-ketopentamethylenecarboxylate, forms colourless crystals, which on warming turn green, then melt, and decompose at 114°.

*$\alpha$ -Oximinopimelic acid*,  $\text{CO}_2\text{H} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$ , obtained from ethyl 2-ketohexamethylenecarboxylate, melts at 142—143°, forms a crystalline *silver hydrogen* salt, and when heated gives an oil which, on hydrolysis, yields adipic acid. *Diethyl bisnitroso-2-ketohexamethylenecarboxylate* forms colourless crystals, which on warming turn green, melt, and decompose at 110°.

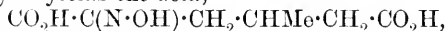
R. H. P.

Nitroso-compounds from Ethyl Methyl 2 ketopentamethylenecarboxylate, obtained by the Condensation of Ethyl  $\beta$  Methyladipate, and their Constitution. By WILHELM DIECKMANN and A. GROENEVELD (*Ber.*, 1900, 33, 595—605. Compare preceding abstract).—Ethyl methyl-2-ketopentamethylenecarboxylate, obtained by the condensation of ethyl  $\beta$ -methyladipate, can be converted into ethyl  $\alpha$ -oximino- $\gamma$ -methyladipate, which in turn can be converted into  $\beta$ -methylglutaric acid, thus showing that the methyl group occupies the 4-position in the condensation product, which has the formula

$$\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CO} \end{array} > \text{CH} \cdot \text{CO}_2\text{Et}, \text{ and not } \begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CO} \end{array} > \text{CH} \cdot \text{CO}_2\text{Et}.$$

*Ethyl  $\alpha$ -oximino- $\beta$  methyladipate*, obtained by treating ethyl 1-methyl-

2-ketopentamethylenecarboxylate with nitrous acid, melts at  $59-60^{\circ}$  and on hydrolysis yields the acid,



which forms colourless crystals melting at  $162-163^{\circ}$ , yields a characteristic *silver hydrogen* salt, and by successive treatment with acetic anhydride and potash yields  $\beta$ -methylglutaric acid.

*Ethyl bisnitroso-4-methyl-2-ketopentamethylenecarboxylate* crystallises in colourless, prismatic needles melting and decomposing at  $94^{\circ}$ ; the corresponding *methyl* ester is very similar and has the same melting point, both yield on hydrolysis  $\alpha$ -oximino- $\gamma$ -methyladipic acid.

R. H. P.

**Acetals from Phenols.** By R. FOSSE (*Compt. rend.*, 1900, 130, 725-727. Compare Claisen, *Abstr.*, 1887, 270; Moureu, *Abstr.*, 1898, i, 660; 1899, i, 30, 493 and 679).—as *Diphenoxyethane*, obtained by heating at  $120^{\circ}$  a dilute alcoholic solution of phenol, ethylidene chloride, and potassium hydroxide and distilling the product under diminished pressure, crystallises from liquid methyl chloride and melts at  $10^{\circ}$ ; at the ordinary temperature, it is an amber-coloured oil having an aromatic odour; it boils at  $174-176^{\circ}$  under 27 mm. pressure and can be distilled in steam.

as *Dinaphthoxyethane*, prepared in a similar manner, crystallises from alcohol in colourless needles melting at  $117^{\circ}$ .

When heated with dilute sulphuric acid, these aromatic acetals are readily hydrolysed into acetaldehyde and the corresponding phenol.

G. T. M.

**Ketone Reactions of Cyclopentadiene.** By JOHANNES THIELE (*Ber.*, 1900, 33, 666-673).—The hydrogen atom in the grouping  $\text{CH}\cdot\text{C}\cdot\text{C}$  has not the same replaceability as in  $\text{CH}\cdot\text{C}\cdot\text{O}$ ; in  $\text{CH}_2(\text{C}\cdot\text{C})_2$ , however, the replaceability is at last equal to that in ketones, as is

exemplified by cyclopentadiene,  $\text{CH}_2\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{smallmatrix}$ . When a mixture of

this substance (Kramer and Spilker, *Abstr.*, 1896, i, 289) with ethyl nitrite is added gradually to alcoholic sodium ethoxide at  $20-30^{\circ}$ ,

*bisisonitrosocyclopentadiene*,  $(\text{OH}\cdot\text{N}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{smallmatrix})_2$ , is formed; it melts and decomposes at  $185-186^{\circ}$ , and yields a *benzoyl* derivative,  $(\text{C}_6\text{H}_5\text{ONBz})_2$ , which melts and decomposes at  $208-209^{\circ}$ . When ethyl

nitrate is used instead of the nitrite, at the ordinary temperature,

*nitrocyclopentadiene*,  $\text{NO}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{smallmatrix}$ , is formed; this substance is

very unstable, but its *sodium* and *silver* derivatives were prepared and analysed; with an alkali diazobenzenesulphonate, it forms a colouring matter. Cyclopentadiene also condenses with ethyl oxalate in the presence of lukewarm alcoholic sodium ethoxide; *ethyl cyclopentadieneoxalate*,  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{smallmatrix}$ , was isolated in the form

of its red sodium derivative, which could not be obtained pure, however; with an alkali diazobenzenesulphonate, it forms a dye. Cyclopentadiene also condenses with acetone, acetophenone, or benzophenone



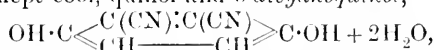
in the presence of sodium ethoxide; the first product boils at  $46^{\circ}$  under 11 mm.,  $153\text{--}154^{\circ}$  under 717 mm. pressure and has a sp. gr. 0.8858 at  $17^{\circ}/4^{\circ}$ ; the second boils at  $130.5^{\circ}$  under 10.5 mm.; the third melts at  $82^{\circ}$ ; they are coloured orange to red, and are more or less unstable in the air. They are named *dimethylfulvene*, *phenylmethylfulvene*, and *diphenylfulvene*, being regarded as derivatives of a hydro-

carbon,  $\text{CH}_2\text{:C} \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix}$ , which is named fulvene because its derivatives are coloured. Evidently the carbon nucleus which it contains is chromophoric in character; it is pointed out that similar nuclei exist in other coloured substances, for example, in quinone and phorone. Cyclopentadiene also condenses with aldehydes to form coloured products, but these are very unstable; *phenylfulvene* is dark red and melts at about  $31^{\circ}$ ; with formaldehyde, which theoretically should yield fulvene itself, no well-defined product could be obtained. With diazobenzene chloride in alkaline solution cyclopentadiene yields a coloured product, but here, again, no well-defined substance could be isolated. C. F. B.

**Solubility of Benzophenone.** By E. DERRIEN (*Compt. rend.*, 1900, 130, 721—723).—Determinations of the solubility of benzophenone in thirty-two organic and inorganic solvents are recorded.

G. T. M.

**Addition of Hydrogen Cyanide to Quinone.** By JOHANNES THIELE and J. MEISENHEIMER (*Ber.*, 1900, 33, 675—676).—When a strong solution of potassium cyanide is added gradually to an alcoholic solution of quinone which contains sulphuric acid in addition, the solution being kept cool, quinol and *o*-dicyanoquinol,



are formed, the latter in yield greater than 70 per cent. This substance is yellowish, and blackens at about  $230^{\circ}$  when anhydrous; it is stable with aqueous acids and alkalis, but when warmed for  $\frac{1}{4}$  hour on the water-bath with concentrated sulphuric acid, is converted to the extent of about 90 per cent. into *p*-dihydroxyphthalimide,

$\text{C}_6\text{H}_2(\text{OH})_2 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{NH} + 3\text{H}_2\text{O}$ , which is yellow, does not melt below  $240^{\circ}$ , and yields *p*-dihydroxybenzoic acid when boiled for several hours with strong hydrochloric acid. Both substances give fluorescent solutions. C. F. B.

**Action of Nitrogen Trioxide on  $\alpha$ -Naphthaquinone.** By JULIUS SCHMIDT (*Ber.*, 1900, 33, 543—547).— $\alpha$ -Naphthaquinone dissolves in liquid nitrogen trioxide (prepared from arsenious anhydride and nitric acid), and after several days thick, dark red crystals of 1:3-diketohydrindene nitrosite,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}\cdot\text{N}_2\text{O}_3$ , separate; this melts and decomposes at  $160^{\circ}$ , gives Liebermann's nitroso-reaction, dissolves in alkalis with a deep red coloration, and slowly decomposes on keeping, with evolution of nitrous fumes. Water at the ordinary temperature converts it into 1:3-diketohydrindene, together with

anhydrobisdiketohydrindene (Wislicenus, Abstr., 1887, 587; with Kötze, *ibid.*, 1889, 1067; with Reitzenstein, Abstr., 1894, i, 133); the latter alone is formed by the action of water at 100°, whilst when the dry nitrosite is heated, phthalic anhydride is obtained.

W. A. D.

Spontaneous Oxidation, "Autoxidation," and Formation of Active Oxygen ("Sauerstoffaktivierung"). By WILHELM MANCHOT (*Chem. Centr.*, 1900, i, 132—133; from *Habilitationsschrift*, Göttingen, 1899).—The products formed by the direct action of oxygen on derivatives of anthracene, phenanthrene, and similar hydrocarbons are much less complex and more easily isolated than those similarly obtained from benzene derivatives. By the action of atmospheric oxygen on oxanthrol in presence of alkali, the red solution becomes colourless, and anthraquinone is formed. When sodium hydroxide is used, nearly half the total quantity of oxygen taking part in the reaction is converted into sodium peroxide. The peroxide was estimated by means of potassium permanganate. When a  $N/4$  solution of barium hydroxide is employed, exactly half the oxygen is found as the peroxide, which separates out, and has no further action on the oxanthrol. Oxidation also takes place with the same rapidity in presence of  $N/4$  solutions of ammonia, potassium cyanide, or sodium carbonate, but only very slowly in presence of water alone, and still more slowly in presence of dilute hydrochloric acid. Ozone is not formed, and light has no effect on the oxidation. Dihydrophenanthraquinone, under similar conditions, passes through the green quinhydrone to the yellowish-red phenanthraquinone, half the oxygen forming peroxide. Hydrochrysenequinone and hydroretenequinone behave like hydrophenanthraquinone; the formation of quinhydrone retards the reaction. The intermediate products of the oxidation of the hydroxybenzenes could not be isolated, but the naphthols yield compounds often contaminated with tar. Phenylhydroxynaphthol forms phenylhydroxynaphthaquinone. By the action of oxygen on hydrazobenzene, peroxide is formed, but the reaction takes place too slowly to allow of its progress being followed. Hydrazomethyltriazole, although having strongly basic properties, is oxidised by air in presence of alkali in a manner precisely similar to that of phenols, peroxide and azo-compounds being formed.

In this process of oxidation, the oxygen first attacks the compounds,  $RH_2$  forming  $R$  and  $H_2O_2$ , the alkali acting as a catalytic agent, and accelerating the action. The formation of salts does not entirely explain the process, for oxanthrol is oxidised much more rapidly when it is shaken with borax or disodium hydrogen phosphate solution than when water alone is used, although ionisation does not take place, for the solution does not become red. The oxidation of hydrazobenzene is very slow in aqueous alcoholic solution, but is considerably accelerated by the addition of alkali. The acid or basic properties of the compound have no influence on the rapidity of oxidation.

The catalytic action of the alkali is of physiological interest in reference to the absorption of oxygen by blood, and the oxidations effected in it.

E. W. W.

**Oxidation of the Nature of Dehydrogenation by means of Ferricyanides: Oxidation of Camphor.** By ALEXANDRE ÉTARD (*Compt. rend.*, 1900, 130, 569—571).—The results of various observers show that when carbon compounds containing nitrogen, such as hydratropine, phenylene-ethylenediamine, aminoacetone and conicine, are oxidised by means of alkali ferricyanides, they lose hydrogen, but not carbon. Similarly, when camphor is treated with an alkali ferricyanide at the ordinary temperature, it is converted into camphoric acid.

It is incorrect to speak of strong and weak oxidising agents; the results of oxidation depend on the relative constitution of the oxidising agent and the substance oxidised. C. H. B.

**Reaction between Aromatic Aldehydes and the Sodium Derivative of Borneol.** By ALBIN HALLER (*Compt. rend.*, 1900, 130, 688—691. Compare Abstr., 1891, 1498; 1899, i, 770).—Benzylidene-*d*-camphor is produced when the sodium derivative of either *d*-borneol or *l*-isoborneol is treated with benzaldehyde; *l*-borneol, however, gives rise to the corresponding derivative of *l*-camphor, the following compounds having been prepared in order to corroborate this observation.

*o*-Methoxybenzylidene-*l*-camphor,  $C_8H_{14} \begin{smallmatrix} C:CH \cdot C_6H_4 \cdot OMe \\ | \\ CO \end{smallmatrix}$ , produced

by adding *o*-methoxybenzaldehyde to a solution of the sodium derivative in light petroleum, melts at 92—94°, and has  $[a]_D - 414.58'$  in alcoholic solution, whereas its optical antipodes, dissolved in toluene, gives +431.50°.

*p*-Methoxybenzylidene-*l*-camphor melts at 125°, and has  $[a]_D - 528.17'$ , whilst the dextrorotatory compound has 467.07°.

*Piperonylidene-l*-camphor crystallises in needles melting at 159.5° and has  $[a]_D - 393.8'$ ; the *d*-modification gives 435.40°.

The discrepancy in the arithmetical values of  $[a]_D$  for the antipodal forms is due to the employment of solutions of varying concentrations in different solvents. G. T. M.

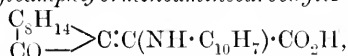
**Resolution of Racemic Benzylidenecamphor.** Isomorphism of the Active Components. By JULES MINGUIN (*Compt. rend.*, 1900, 130, 510—513. Compare Abstr., 1897, i, 163, and 1899, i, 771).—When a crystal of dextrorotatory benzylidene camphor is introduced into a supersaturated toluene solution of the racemic compound, optically active crystals separate which appear to contain variable proportions of the two active components; the specific rotation of the dextrorotatory crystals varies from 178° to 310°, and that of the levorotatory crystals from -130° to -262°; the active compound has  $[a]_D \pm 430°$ . The two components appear to exist in the same crystal in an unracemised condition, for the mixed crystals, like those of the optically active components, belong to the orthorhombic system, whereas the racemic compound crystallises in the monoclinic system. A levorotatory crystal induces crystallisation in a supersaturated alcoholic solution of the dextrorotatory compound probably because

the racemic compound which is formed is insoluble under these conditions; the addition of a racemic crystal produces no effect and in toluene solutions negative results are obtained in both cases.

The optically active crystals obtained in these experiments melt indefinitely at  $78-90^\circ$ ; mixtures of the two antipodes behave in a similar manner, whereas the racemic compound melts at  $78^\circ$  and its active components at  $96^\circ$ .  
G. T. M.

**The Vinylamine of the Camphor Group.** By PAUL DUDEN and ALFRED E. MACINTYRE (*Ber.*, 1900, **33**, 481—483).—When amino-borneol is treated with phosphorus pentachloride, it is converted into 1-chloro-2-camphanamine,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH}_2 \\ | \\ \text{CHCl} \end{smallmatrix}$ ; on covering this base with sodium hydroxide solution, it loses hydrogen chloride, and is converted into camphenamine,  $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{NH}_2 \\ | \\ \text{CH} \end{smallmatrix}$ , which readily takes up hydrogen chloride again, and is reconverted into the chloro-base. In favour of the vinylamine constitution for the base, it is urged that (1) it is unsaturated towards alkaline permanganate; (2) the molecular refraction corresponds with one ethylene linking; (3) it interacts with methyl iodide to form a trimethylcamphenamine iodide,  $C_{10}H_{15} \cdot \text{NMe}_3\text{I}$ ; and (4) it reacts with benzaldehyde (1 mol.) to form a benzylidene compound,  $C_{10}H_{15} \cdot \text{N} \cdot \text{CHPh}$ . Benzenesulphocamphenamide,  $C_{10}H_{15} \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$ , crystallises from a mixture of ether and light petroleum in rhombic tablets and melts at  $95-96^\circ$ ; it is practically insoluble in normal sodium hydroxide solution, but an excess of 6—7 per cent. alkali converts it very largely into the sodium salt, which separates in felted needles; the whole of the amide can be extracted from the alkaline mother liquor by adding ether.  
T. M. L.

**Action of Ethyl Oxalate on Camphor. V.** By JOHN BISHOP TINGLE and ALFRED TINGLE (*Amer. Chem. J.*, 1900, **23**, 214—230. Compare *Trans.*, 1890, 652; *Abstr.*, 1897, i, 484; 1898, i, 443; 1899, i, 444).— $\alpha$ -Naphthylcamphorformeneaminecarboxylic acid,



formed by the action of camphoroxalic acid (1 mol.) on  $\alpha$ -naphthylamine (0.5 mol.) in alcoholic solution, crystallises from benzene in well-developed, amber prisms containing  $\frac{1}{2}$  mol.  $C_6H_6$ ; at  $100-105^\circ$ , the crystals become opaque, then change to a yellow powder which melts and decomposes at  $170^\circ$ . The acid readily dissolves in sodium carbonate solution, but gives no coloration with ferric chloride and alcohol.

$\beta$ -Naphthylcamphorformeneaminecarboxylic acid, obtained in a manner similar to the  $\alpha$ -derivative, crystallises from toluene in bright yellow needles melting and decomposing at  $173^\circ$ .

Orthophenylenediamine condenses with camphoroxalic acid, forming a compound,  $C_{18}H_{20}O_2N_2$ , which crystallises from benzene in bright

yellow needles melting at  $246^{\circ}$ ; it dissolves slightly in hot water, boiling hydrochloric acid, or sodium hydroxide solution, being practically unacted on by these solvents; concentrated sulphuric acid readily dissolves it in the cold, giving a red coloration.

With semicarbazide hydrochloride, camphoroxalic acid yields two compounds of the composition  $\text{C}_8\text{H}_{14}\text{O} \rightarrow \text{C}:\text{C}(\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{H}$ . The

$\alpha$ -semi-carbazide separates from acetone in small, white needles, melting and decomposing at  $218^{\circ}$ ; it is soluble in warm sodium carbonate solution, and is reprecipitated in a gelatinous condition on the addition of acid; it gives no coloration with ferric chloride and alcohol, and does not evolve ammonia when heated with caustic alkali solution. The  $\beta$ -isomeride is precipitated from glacial acetic acid solution by the addition of alcohol in the form of cubical aggregates of colourless, microscopic needles, which melt and decompose at  $209$ – $210^{\circ}$ ; it behaves similarly to the  $\alpha$ -compound with ferric chloride and with sodium carbonate, and from solution in the latter, acids precipitate the  $\alpha$ -compound.

Ethyl camphoroxalate condenses with aniline hydrochloride in presence of alcoholic potash, yielding ethyl phenylcamphorformeneamine-carboxylate,  $\text{C}_8\text{H}_{14}\text{O} \rightarrow \text{C}:\text{C}(\text{NHPh})\cdot\text{CO}_2\text{Et}$ , which crystallises from benzene in almost white, microscopic needles, melting and decomposing at  $158$ – $160^{\circ}$ .

Ethyl  $\beta$ -naphthylcamphorformeneaminecarboxylate,  $\text{C}_{21}\text{H}_{22}\text{ON}\cdot\text{CO}_2\text{Et}$ , is obtained in a similar manner, using  $\beta$ -naphthylamine in place of aniline; it crystallises from benzene in colourless, microscopic needles which soften at about  $160^{\circ}$  and melt and decompose at about  $174^{\circ}$ , the melting point varying with the rapidity of heating.

Ethyl semicarbazylcamphorformeneaminecarboxylate,  $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}_3\cdot\text{CO}_2\text{Et}$ , prepared by condensing ethyl camphoroxalate with semicarbazide hydrochloride in presence of potassium acetate and alcohol, dissolves readily in chloroform, ether, or ethyl acetate; from the last-named solvent, it separates in colourless needles melting at  $202^{\circ}$ .

Phenylcamphorformeneamine reacts with benzoyl chloride in presence of a little sodium hydroxide, yielding a compound which crystallises from benzene in cruciform aggregates of prisms melting at  $160$ – $161^{\circ}$ . With phenylsulphonic chloride, the amine gives a substance, crystallising from benzene in colourless needles, melting at  $133^{\circ}$ . The action of acetic anhydride on the amine gives rise to a compound which separates from a mixture of ethyl acetate and light petroleum in colourless crystals which could not be obtained free from resinous matter; it melts at  $134^{\circ}$ .

T. H. P.

**Genesis of Compounds of the Menthol Series in Plants.**  
By EUGÈNE CHARABOT (*Compt. rend.*, 1900, 130, 518–519. Compare this vol., ii, 101, 241).—Specimens of the essential oil of *Mentha piperita*, obtained from the plant in three stages of growth, were analysed, with the results given on p. 304.

At the commencement, the oil is very rich in free menthol, and

	Oil extracted from the plant before budding.	Oil extracted after the formation of buds.		Oil extracted from the plant in flower.
		(a) Leaves.	(b) Inflorescence	
Sp. gr. at 18° .....	0.9025	0.9016	0.9081	0.9200
Rotatory power at 18°. <i>l</i> = 100 mm.	-21°10'	-26°	-20°15'	-2°37'
Menthylesters (calculated to menthyl acetate) ...	3.7 per cent.	10.3 per cent.	7.5 per cent.	10.7 per cent.
Combined menthol	2.9 "	8.1 "	5.9 "	8.4 "
Free "	14.3 "	12.2 "	29.9 "	32.1 "
Total "	47.2 "	50.3 "	35.8 "	40.5 "
Menthone ... ..	5.2 "	4.2 "	16.7 "	10.2 "

contains only a small amount of menthone; as the green parts develop, the quantity of combined menthol increases. The results obtained with the third sample of oil indicate that the accumulation of esters takes place only in the leaves, and that, as the oil passes to the flowering parts, the amount of esters diminishes; at the same time, the quantity of menthone increases. The menthol, which is produced during the development of the green parts of the plant, becomes esterified in the leaves, and undergoes oxidation to menthone in the inflorescence. The formation of the latter compound depends on the flowering of the plant; when the reproductive functions are arrested by the action of certain insects, the amount of ketone produced is very small.

G. T. M.

**Benzenesulphamino-compounds of Primary Bases.** By RICHARD WILLSTÄTTER and RUDOLF LESSING (*Ber.*, 1900, **33**, 557—559).—Benzenesulphonic chloride reacts with certain primary bases of the terpene group to form amino-compounds, which, in contradiction to Hinsberg's rule, are insoluble in alkalis. *Benzenesulphondihydrocarvylamide*,  $C_{10}H_{17} \cdot NH \cdot SO_2Ph$ , crystallises in colourless needles melting at 132°, and is not altered by concentrated aqueous soda. *Benzenesulphondihydroeucarvylamide* crystallises in quadratic tablets melting at 103—105°, and is also insoluble in alkalis.

A. H.

**Curangin, the Glucoside of Curanga Amara.** By S. E. BOORSMA (*Chem. Centr.*, 1900, i, 298; from *Ned. Tijds. Pharm.*, **11**, 366—371. Compare this vol., i, 243).—Curangagenin,  $C_{30}H_{47}O_7$ , does not contain methoxy-groups. The formula was confirmed by molecular weight determinations. Curangin is either non-poisonous or only very slightly poisonous.

E. W. W.

**Aloe-emodin and Frangula-emodin.** By O. A. OESTERLE (*Arch. Pharm.*, 1899, **237**, 699—704).—Emodin extracted from *Frangula* bark crystallises in orange-red needles and melts at 250°. It can also be distinguished from aloe-emodin (*Abstr.*, 1899, i, 538) by heating it for a little while with strong sulphuric acid, bringing a few drops of the mixture into water, and making alkaline with ammonia, when a cherry-red solution is formed, which gives an absorption band between 0.56 and 0.47 $\mu$ . Under similar circumstances,

aloe-emodin yields a distinctly violet solution, with an absorption band between  $0.59$  and  $0.49\mu$ .

When heated with propionic anhydride, aloe-emodin yields a yellow *product* melting at  $152$ — $153^\circ$ ; the *product* from frangula-emodin melts at  $121$ — $122^\circ$ . When treated with benzoyl chloride and sodium hydroxide, aloe-emodin yields a *tribenzoyl* derivative, whilst frangula-emodin gives a *dibenzoyl* derivative; these are yellow, and melt at  $235^\circ$  and  $225^\circ$  respectively. C. F. B.

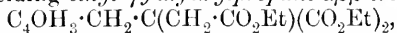
**Cause of the Change of Colour of Congo Red by the Action of Acids.** By ST. SCHIMANSKY (*Chem. Centr.*, 1900, i, 423; from *Mitt. Technol. Gewerb.-Mus. Wien*, 1900, 39—40).—By the action of acids on Congo red, it becomes blue, but this is not due, as hitherto supposed, to the formation of the free dye, but rather to the production of an unstable hydrogen chloride compound, which is gradually decomposed by washing with water. The free dye, which is brownish-red and soluble in water, is prepared by treating a solution with excess of hydrochloric acid, and washing the precipitate with water, until the filtrate acquires a pale pink colour. E. W. W.

**A Glycol and Aldol of the Furfuran Series.** By GUSTAV LINDAUER (*Monatsh.*, 1900, 21, 72—79).—Furfuraldehyde and isobutaldehyde condense in the presence of alcoholic potash to form  $\gamma$ -furfuryl- $\beta\beta$ -dimethylpropylene glycol,  $C_4OH_3 \cdot CH(OH) \cdot CMe_2 \cdot CH_2 \cdot OH$ , which is a hygroscopic, colourless substance, melts at  $64^\circ$ , is volatile with steam, and boils at  $257^\circ$  (corr.). The *diacetate* is a colourless liquid, which boils at  $176$ — $177^\circ$  under 42 mm. pressure. The two aldehydes, when shaken together with a cold saturated solution of potassium carbonate, form a thick oil, which cannot be distilled, and is probably the *aldol* corresponding with the above glycol, which is formed when this oil is reduced by means of aluminium amalgam. R. H. P.

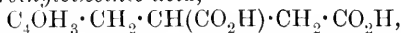
**Furfuroylacetic Acid and Methyl Furfuryl Ketone.** By S. S. SANDELIN (*Ber.*, 1900, 33, 492—494. Compare Marquis, *Abstr.*, 1899, i, 798).—Ethyl furfuroylacetate,  $C_4OH_3 \cdot CO \cdot CH_2 \cdot CO_2Et$ , may be obtained by the action of sodium on a mixture of ethyl acetate and ethyl pyromucate, according to Claisen and Lowman's method (*Abstr.*, 1887, 583); it is an almost odourless, greenish-yellow oil distilling at  $170^\circ$  under 33 mm. pressure; its *copper* derivative,  $C_{18}H_{18}O_8Cu$ , is a green, microcrystalline powder melting at  $175^\circ$ . When the ester is warmed for several hours on the water-bath with a slight excess of phenylhydrazine, it yields 1-phenyl-3-furfurylpyrazolone,  $NPh \cdot \begin{matrix} N=C \cdot C_4OH_3 \\ \diagup \quad \diagdown \\ CO \cdot CH_2 \end{matrix}$ , crystallising in colourless plates and melting at  $179^\circ$ , and when boiled with sulphuric acid (1 in 25) for some  $2\frac{1}{2}$  hours, and then extracted with ether, it yields methyl furfuryl ketone melting at  $33^\circ$  and distilling at  $173^\circ$ , the phenylhydrazone of which melts at  $86.5^\circ$  and the *oxime* at  $92^\circ$ . When the oxime is treated with Beckmann's mixture, it yields a small quantity of a nitrogen compound melting at  $108^\circ$ , which, when hydrolysed with potassium hydroxide, yields a compound melting at  $99^\circ$ . J. J. S.

**Furysuccinic Acid** [**Furfurysuccinic Acid**]. By S. S. SANDELIN (*Ber.*, 1900, 33, 487—489. Compare Abstr., 1898, i, 467).—*Ethyl β-cyano-β-furfurylpropionate*,  $C_4OH_3 \cdot CH(CN) \cdot CH_2 \cdot CO_2Et$ , is formed when ethyl furfurylmalonate is heated for 7 hours at 60° with an aqueous alcoholic solution of potassium cyanide (1 mol.); it distils at 174·5° under 33 mm. pressure, readily turns brown, and, on hydrolysis with an excess of barium hydroxide, yields furfurylsuccinic acid. *β-Cyano-β-furfurylpropionic acid* is obtained, together with considerable amounts of bye-products, when 2 mols. of potassium cyanide are employed; it crystallises from benzene in needles melting at 109°, dissolves in water, but is insoluble in light petroleum, and is readily hydrolysed to the succinic acid; its *calcium* and *barium* salts are readily soluble in water, whereas the *silver* salt is insoluble, but readily decomposes. When dissolved in hot water, it is hydrolysed to *furfurylsuccinamic acid*,  $C_4OH_3 \cdot CH(CO \cdot NH_2) \cdot CH_2 \cdot CO_2H$ , which crystallises in colourless needles melting at 155°. The *diamide*, obtained by the action of concentrated ammonia on the methyl ester, crystallises from boiling water in thin plates melting and decomposing above 220°; the *dihydrazide* forms a white powder melting at 159—161°, dissolves readily in water, and yields a *dibenzylidene* derivative,  $C_{22}H_{20}O_3N_4$ , melting at 199—200°. J. J. S.

**Furfurylsuccinic Acid** [**Furfurylcarbinylsuccinic Acid**]. By S. S. SANDELIN (*Ber.*, 1900, 33, 489—491).—*Ethyl furfurylcarbinylmalonate*, obtained from the acid (Abstr., 1888, 678) by the aid of sulphuric acid and alcohol, is a pale yellow oil distilling at 171—173° under 33 mm. pressure; it reacts with sodium ethoxide and ethyl chloroacetate, yielding *ethyl γ-furfurylpropane-αβ-tricarboxylate*,



which is a thick, yellowish oil distilling at 212—213·5° under 25 mm. pressure; when hydrolysed with excess of alcoholic potash, it yields the *acid*, which, after solution in ether and precipitation with light petroleum, forms minute needles melting and decomposing at 155—156°. When the acid is heated at 155—160°, it loses carbon dioxide and yields *furfurylcarbinylsuccinic acid*,



crystallising from acetic acid in plates melting at 139·5—140° and insoluble in benzene, chloroform, or light petroleum; the *ethyl* ester is a pale yellow oil distilling at 213·5—215° under 67 mm. pressure.

J. J. S.

**Hydroxylamine Derivatives of Tetrahydropyrone Compounds.** By PAVEL IW. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 901—905, and *Ber.*, 1900, 33, 744—747. Compare Abstr., 1899, i, 706).—*o*-Diethoxydiphenyltetrahydropyroneoxime crystallises with various organic liquids, giving the following compounds. With glycerol, in which it is only slightly soluble,  $C_{21}H_{25}O_4N + C_3H_8O_3$ , which melts at about 126°. Ethylene glycol readily dissolves the oxime, and deposits shining crystals of the composition  $C_{21}H_{25}O_4N + 2\frac{1}{2}C_2H_6O_2$ , which melt, when quickly heated, at about 106°. Benzene yields efflorescent crystals of the formula  $C_{21}H_{25}O_4N + 1\frac{1}{2}C_6H_6$ , and with carbon tetrachloride the compound  $C_{21}H_{25}O_4N + 2CCl_4$  is formed. With quinoline,  $C_{21}H_{25}O_4N + 2C_9H_7N$ , melting at about 104°, is obtained, and



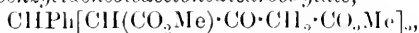
aniline gives  $C_{21}H_{25}O_4N + 2\frac{1}{2}C_6H_7N$ . Compounds were also obtained with ethyl malonate, ethyl acetoacetate, ether, amyl alcohol, isovaleric acid, ethylene bromide, and nitrobenzene, but in all these cases crystals deposited at different temperatures did not give concordant numbers on analysis.

o-Dimethoxydiphenyltetrahydropyroneoxime crystallises with ethyl malonate, ethyl acetoacetate, or acetic acid, forming compounds of indefinite composition.

Diphenyltetrahydropyroneoxime is readily dissolved by ethylene glycol, and the solution deposits shining crystals having the composition  $C_{17}H_{17}O_2N + 2C_2H_6O_2$  and melting at  $145^\circ$ . With glycerol, it gives shining needles of the formula  $C_{17}H_{17}O_2N + C_3H_8O_3$ , and melting at  $147^\circ$ . With ethyl malonate and ethyl acetoacetate, indefinite compounds are obtained.

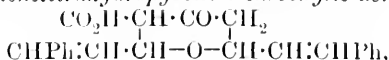
The benzoyl derivative of diphenyltetrahydropyroneoxime,  $O\langle\begin{smallmatrix} CHPh\cdot CH_2 \\ CHPh\cdot CH_2 \end{smallmatrix}\rangle C:N\cdot OBz$ , separates from acetic acid solution in white crystals which melt at  $157^\circ$  and dissolve slightly in alcohol, but are insoluble in water. T. H. P.

**Synthesis of Tetrahydropyrone Derivatives.** By PAVEL IW. PETRENKO-KRITSCHENKO and E. ELTCHANINOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 905—909. Compare Abstr., 1899, i, 440).—On condensing benzaldehyde with ethyl acetonedicarboxylate in presence either of hydrochloric acid or ammonia, a mixture of isomeric ethyl diphenyltetrahydropyronecarboxylates is obtained with melting point varying from  $116$ — $126^\circ$ ; the solubilities of these isomerides are apparently nearly equal, since they could not be separated by crystallisation. When methyl acetonedicarboxylate is used instead of the ethyl ester in this condensation, in presence of hydrochloric acid, the corresponding methyl derivative, having the composition  $C_{21}H_{20}O_6$ , and the melting point  $194^\circ$ , is obtained; when ammonia is used as the condensing agent, an isomeric compound melting at  $146$ — $149^\circ$  is obtained, which, however, could not be separated from a small quantity of an admixed isomeride. In presence of a few drops of diethylamine, benzaldehyde and methyl acetonedicarboxylate condense to form methyl benzylidenebisacetonedicarboxylate,



which melts at  $167$ — $172^\circ$ , and is slightly soluble in alcohol, chloroform, or benzene, but insoluble in water; its alcoholic solution gives a faint red colour with ferric chloride. T. H. P.

**Bis-Phenylethylenetetrahydropyronecarboxylic Acid and its Derivatives.** By EDOARDO COEN (*Gazzetta*, 1900, 30, i, 1—8).—2 : 5-Diphenylethylenetetrahydropyrone-3-carboxylic acid,



obtained by passing hydrogen chloride into a mixture of 2 mols. of cinnamaldehyde and one of acetonedicarboxylic acid dissolved in acetic acid, separates from benzene as an orange-yellow powder and melts at  $210$ — $211^\circ$ ; it is soluble in alcohol, ether, or ethyl acetate. The bromo-derivative,  $C_{22}H_{19}O_4Br$ , separates from alcohol as a yellow powder melting and decomposing at above  $280^\circ$ , and dissolves in benzene or ether, and, to

a less extent, in alcohol. The *ethyl* ester of the acid,  $C_{24}H_{24}O_4$ , is precipitated from benzene solution, by the addition of light petroleum, as a yellow powder melting at  $233^\circ$ . By the action of alcoholic ammonia on the ethyl ester, three isomeric *bases*, of the composition  $C_{41}H_{41}O_7N$ , are obtained. The first of these is a yellow substance, and when crystallised from alcohol melts at  $244$ – $245^\circ$ ; the second is soluble in ethyl acetate and melts at above  $280^\circ$ ; and the third is insoluble in all solvents. They yield pale yellow, crystalline *platini-chlorides*.  
T. H. P.

**2-Methyl-7-hydroxypheno-3-pyrone** (2-Methyl-7-hydroxychromone). By M. BLOCH and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 471–476).—The name "*chromone*" is introduced for pheno- $\gamma$ -pyrone,  $C_6H_4 \begin{smallmatrix} O-CH \\ || \\ CO \cdot CH \end{smallmatrix}$ .

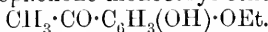
*a*-Acetyl-2:4 diethoxyacetophenone,  $CH_3Ac \cdot CO \cdot C_6H_4(OEt)_2$ , is prepared by the action of ethyl acetoacetate on resacetophenone diethyl ether, crystallises from dilute alcohol in colourless prisms, melts at  $90^\circ$ , and gives a red coloration with ferric chloride in alcoholic solution. When heated with hydriodic acid, it gives 7-ethoxy-2-methylchromone,

$OEt \cdot C_6H_3 \begin{smallmatrix} O-CMe \\ || \\ CO \cdot CH \end{smallmatrix}$ , which crystallises from dilute alcohol in broad,

silky needles, melts at  $123$ – $124^\circ$ , and gives a violet-blue fluorescence when dissolved in sulphuric acid. In this respect, it resembles

3:7-diethoxychromone,  $OEt \cdot C_6H_3 \begin{smallmatrix} O-CH \\ || \\ CO \cdot C \cdot OEt \end{smallmatrix}$ , the diethyl ether of

Schall and Dralle's oxidation product of brazilin (*Abstr.*, 1892, 502; compare Feuerstein and Kostanecki, *Abstr.*, 1899, i, 538), which crystallises in large, flat needles, and melts at  $125^\circ$ . When heated with sodium ethoxide, 7-ethoxy-2-methylchromone is hydrolysed into acetic acid and resacetophenone monoethyl ether,



7-Hydroxy-2-methylchromone,  $OH \cdot C_6H_3 \begin{smallmatrix} O-CMe \\ || \\ CO \cdot CH \end{smallmatrix}$ , is produced in the action of hydriodic acid on acetyldiethoxyacetophenone, along with the ethyl ether already described, from which it can be prepared by the further action of hydriodic acid; it crystallises from dilute alcohol in short, thick, well-formed, microscopic prisms, melts at  $249$ – $250^\circ$ , and gives a blue-violet fluorescence when dissolved in sulphuric acid.

T. M. L.

**Condensation of Homologous Phloroglucinols with Salicylaldehyde.** By HUGO WEIDEL and FRANZ WENZEL (*Monatsh.*, 1900, 21, 62–71).—When dimethylphloroglucinol and salicylaldehyde, dissolved in acetic acid, are heated together with hydrochloric acid, crystals containing hydrochloric acid separate out, which, on treatment with water, decompose and leave 5:7-dimethyl-8-hydroxyfluorone; this crystallises in dark red prisms melting at  $275^\circ$  and yields an *acetyl* derivative, which forms clusters of lustrous, yellow needles, and melts at  $208$ – $210^\circ$ ; on treatment with potash and methyl iodide, it forms a *pseudomethyl ether*, which crystallises in dull, orange-yellow needles melting at  $133^\circ$ .

Methylphloroglucinol and salicylaldehyde form a similar condensation product, (5-or 7-)*methyl-8-hydroxyfluorone*, which is a very insoluble substance crystallising only from methyl alcohol in ochreous, microscopic needles melting and decomposing at  $220^{\circ}$ .

R. H. P.

**Ricinine.** By THOMAS EVANS (*J. Amer. Chem. Soc.*, 1900, 22, 39—46. Compare Tuson, *Trans.*, 1864, 17, 195, *Werner Jahresber.*, 1870, 877, and Schulze, *Abstr.*, 1898, i, 42).—It appears that the compounds obtained by Tuson and by Schulze are identical; Tuson's method of extraction yields somewhat less satisfactory results than Schulze's, although the product obtained is lighter in colour. It has been found advantageous to substitute boiling toluene for alcohol in Tuson's method. When recrystallised from alcohol, ricinine forms small plates melting at  $193^{\circ}$ . The analytical data agree fairly well with those obtained by Schulze and point to the composition  $C_{16}H_{16}O_4N_4$ .

A *dibromide*, probably  $C_{16}H_{16}O_4N_4Br_2$ , or  $C_{16}H_{14}O_4N_4Br_2$ , is obtained when ricinine is treated with bromine in either aqueous or chloroform solution; it crystallises in long, brittle needles melting and decomposing at  $230^{\circ}$ , and is only sparingly soluble in most solvents. Alkaline potassium permanganate readily oxidises ricinine, yielding an acid which crystallises in colourless needles melting at  $279$ — $280^{\circ}$ , but turns black a few degrees lower. A second oxidation product crystallising in red prisms and soluble in benzene to a reddish-yellow solution with a green fluorescence has also been obtained. J. J. S.

**Chloro-derivatives of Oxygenated Alkaloids. Action of Chlorine on Strychnine in Glacial Acetic Acid Solution.** By GAETANO MINUNNI and GIOVANNI ORTOLEVA (*Gazzetta*, 1900, 30, i, 39—54).—The principal product obtained by passing chlorine into an acetic acid solution of strychnine is a *tetrachlorostrychnine*,  $C_{21}H_{18}O_2N_2Cl_4 + H_2O$ , which separates from alcohol in white, prismatic crystals soluble in glacial acetic acid, and very slightly so in alcohol; its *hydrochloride* dissolves in acetic acid. It forms an *oxime*,  $C_{21}H_{18}ON_2Cl_4 \cdot N \cdot OH + 2H_2O$ , which at  $160^{\circ}$  loses  $\frac{1}{2}H_2O$  and begins to decompose; it is soluble in alkali hydroxide solution, and is reprecipitated by acids. The *hydrochloride* of the oxime,  $C_{21}H_{19}O_2N_3Cl_4 \cdot HCl + 2\frac{1}{2}H_2O$ , is slightly soluble in boiling alcohol, from which it may be crystallised.

Besides the tetrachloro-derivative, a small quantity of a *hexachlorostrychnine*,  $C_{21}H_{16}O_2N_2Cl_6$ , is also obtained; it is a white compound readily soluble in glacial acetic acid.

T. H. P.

**Pyrrolealdehyde.** By EUGEN BAMBERGER and G. DJERDJIAN (*Ber.*, 1900, 33, 536—542).—Reimer's reaction takes place with pyrrole, giving rise to *pyrrole-2-aldehyde*,  $\begin{array}{c} \text{CH} \cdot \text{NH} \\ | \\ \text{CH} \cdot \text{CH} \end{array} \geq \text{C} \cdot \text{CHO}$ ; (this melts at  $45^{\circ}$ ;

and, unlike benzaldehyde, forms large, colourless, rhombic crystals, is odourless, does not redden magenta which has been decolorised by sulphurous acid, and is not oxidised by the air; with alkaline potassium permanganate, it yields pyrroline-2-carboxylic acid (Ciamician and Silber, *Abstr.*, 1884, 1041), a fact which determines its structure. The sodium hydrogen sulphite derivative,  $C_4H_6O_4NSNa$ , crystallises

from water in lustrous leaflets, and the *phenylhydrazone* from light petroleum in white, shining needles melting at  $139-139.5^\circ$ ; the *p*-nitrophenylhydrazone crystallises from xylene in reddish-black needles with an intense, steel-blue surface-colour, and melts at  $182.5-183^\circ$ . The author emphasises the fact that the latter compound gives brownish-yellow solutions with chloroform, xylene, carbon tetrachloride, or ether, although with methyl or ethyl alcohol, glacial acetic acid, or ethyl acetate dark red solutions are obtained; the explanation is, perhaps, to be sought for in the different dissociating powers of the solvents named. The *p*-nitrophenylhydrazones of a large number of other ketones and aldehydes show a similar behaviour; that derived from diacetyl,  $C_{10}H_{11}O_3N_3$ , hitherto undescribed, forms orange-yellow needles with a silky lustre, and melts at  $229.5-230.5^\circ$ . *Pyrrrole-aldoxime* crystallises from chloroform or benzene in white, silky needles and melts at  $164.5^\circ$ .  
W. A. D.

**Derivatives of 5:6:8-Trimethylquinoline.** By HJALMAR WIKANDER (*Ber.*, 1900, 33, 646-648).—5:6:8-Trimethylquinoline methiodide,  $C_{12}H_{13}NMeI$ , crystallises from water in large, yellow, prismatic rods and needles melting and decomposing at  $208-209^\circ$ . The methiodichromate,  $(C_{12}H_{13}NMe)_2Cr_2O_7$ , separates from aqueous solution in small, yellow, sparkling needles which darken at  $206^\circ$  and explode at  $216^\circ$ . The methochloride,  $C_{12}H_{13}NMeCl + 1\frac{1}{2}H_2O$ , dissolves in alcohol, and on precipitating with ether separates in small, bluish-green, prickly prisms which soften at  $82^\circ$  and melt at  $135^\circ$ . The base yields a dibromide,  $C_{12}H_{13}NBr_2$ , which crystallises from acetic acid in large, dark yellow, needles.

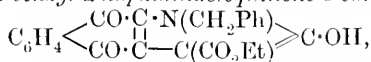
5:6:8-Trimethyltetrahydroquinoline,  $C_{12}H_{17}N$ , obtained by reducing the trimethylquinoline, is a thick, strongly-smelling oil, boiling at  $287-290^\circ$ . Its hydrochloride crystallises from water in a felt-like mass of small needles which soften at  $230^\circ$  and melt and decompose at  $238-239^\circ$ .  
T. H. P.

**Syntheses of 2- and 4-Hydroxyquinolines.** By RUDOLF CAMPS (*Arch. Pharm.*, 1899, 237, 659-691).—Most of the results detailed in this paper have been already published (this vol., i, 115), but the following compounds appear to have been described for the first time. *Propionyl-o-flavaniline* is yellowish, and melts at  $137^\circ$ ; *butyryl-o-flavaniline* is white, and melts at  $104^\circ$ . 2-Hydroxy-4-methyl-3-ethylquinoline melts at  $226^\circ$ ; 4-hydroxy-2-propylquinoline melts at  $166^\circ$ , and the orange *platinichloride* melts and decomposes at  $228^\circ$ . 2-Hydroxy-4-phenylquinoline melts at  $259^\circ$ , and has only feeble acid and basic properties; when distilled with zinc-dust in a current of hydrogen gas, it yields 4-phenylquinoline.  
C. F. B.

**Malonic Acid Derivatives of Dibromo- $\alpha$ -naphthaquinone.** By CARL T. LIEBERMANN [and in part E. HOYER] (*Ber.*, 1900, 33, 566-578. Compare Abstr., 1899, i, 522).—Ethylamine 1-ethyl-naphthindolinonequinone-3-carboxylate forms lustrous, steel-blue prisms; the sodium salt crystallises in the form of dark blue needles, and the copper salt is precipitated as red clots from a solution of copper acetate.  $\alpha$ -Bromonaphthaquinone-3-ethylacetamide, obtained as a bye-product in

the formation of ethyl ethylnaphthindolinonequinonecarboxylate, (*loc. cit.*) forms red prisms. This ester, on hydrolysis, yields 2-hydroxy-1-ethylnaphthindolequinone,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{N} \text{Et} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH} \end{smallmatrix} > \text{C} \cdot \text{OH}$ , which from its solution in caustic alkalis is precipitated by acids as a blue powder closely resembling indigotin as regards its solubilities and behaviour with sulphuric acid; it does not, however, colour mordants.

*Ethyl 2-hydroxy-1-benzyl- $\alpha$ -naphthindolequinone-3-carboxylate*,



prepared by the action of benzylamine on ethyl 2-bromo- $\alpha$ -naphthaquinone-3-malonate, forms yellow, silky needles, which melt about  $160^\circ$ , colours mordants, and, on hydrolysis, yields 2-hydroxy-1-benzyl- $\alpha$ -naphthindolequinone.

Ethyl bromo- $\alpha$ -naphthaquinoneacetoacetate condenses with ethylamine to form the *ethylamide* of 2-methyl-1-ethylnaphthindolequinone-3-carboxylic acid,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{N} \text{Et} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{C}(\text{CO} \cdot \text{NH} \text{Et}) \end{smallmatrix} > \text{C} \text{Me}$ , which forms lustrous, dark steel-blue needles.

*2-Hydroxy- $\alpha$ -naphthaquinone-3-acetic acid*,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{OH} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , prepared by treating ethyl bromo- or chloro- $\alpha$ -naphthaquinonemalonate with alkalis, forms bright yellow tablets, which melt at  $206-207^\circ$ ; the *sodium*, *copper*, and *ethylamine* salts were prepared and analysed; the *monomethyl* ester forms bright yellow needles melting at  $144-145^\circ$ .

By the action of alcoholic potash on ethyl bromonaphthaquinoneacetoacetate, a *compound*,  $C_{13}H_9O_3Br$ , is obtained as a yellow, crystalline substance melting at  $134^\circ$ ; its solutions in alkali hydroxides or carbonates show strong fluorescence. Its *monoethyl* ester melts at  $180^\circ$ , the *monomethyl* ester at  $158^\circ$ , but neither exhibit the fluorescence of the parent substance.

*Ethyl  $\alpha$ -naphthaquinonedimalonate*,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et})_2 \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et})_2 \end{smallmatrix}$ , forms yellow crystals which melt at  $98^\circ$  and dissolve in alkalis with green fluorescence; alkalis convert it into *ethyl  $\alpha$ -naphthaquinoneisoidinedicarboxylate*,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et}) \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix} > \text{CO}$ , which crystallises in dark green needles with a violet iridescence.

*Ethyl 2-acetonyl- $\alpha$ -naphthaquinone-3-acetate*,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{COMe} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ , prepared by leaving a mixture of dibromonaphthaquinone (1 mol.), ethyl acetoacetate (1 mol.), and sodium ethoxide (2 mols.) overnight, crystallises in red needles melting at  $158^\circ$ . R. H. P.

**Action of Iodine on Antipyrine.** By J. BOUGAULT (*J. Pharm.*, 1900, [vi], 11, 97-100).—The author's method for the estimation of antipyrine (Abstr., 1899, ii, 193) is also applicable to the estimation

of hypnal and salipyrine, 1 gram of the former absorbing 0.7185 gram of iodine, and 1 gram of the latter 0.7791 gram of iodine.

When concentrated alcoholic solutions of 4 mols. of antipyrine, 4 mols. of iodine, and 3 mols. of mercuric chloride are heated to 70—80° and then mixed together, the compound  $4C_{11}H_{11}ON_2I, HgCl_2, HgI_2, 2HCl$  is gradually deposited as a light yellow, crystalline powder. If, however, only 2 mols. of mercuric chloride are used for every 4 mols. of antipyrine, then the bright yellow, crystalline compound,  $2C_{11}H_{11}ON_2I, HgI_2, HCl$ , is obtained. H. R. LE S.

Iodoantipyrine. By J. BOUGAULT (*J. Pharm.*, 1900, [vi], 11, 100—102. Compare Abstr., 1886, 158).—Pure iodoantipyrine may be obtained by decomposing the compound  $4C_{11}H_{11}ON_2I, HgCl_2, HgI_2, 2HCl$  with a solution of potassium iodide made alkaline with a little sodium carbonate. It may also be readily prepared by adding iodine, dissolved in a solution of potassium iodide, to a boiling solution of antipyrine and sodium acetate in water. On cooling the mixture, the iodoantipyrine is precipitated in almost theoretical amount.

100 c.c. of water at 17° dissolve 0.080 gram of antipyrine.

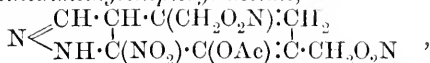
H. R. LE S.

1-Phenyl-4-methylpyrazolone. By FRITZ FICHTER, JOSEPH ENZENAUER, and EMIL UELLENBERG (*Ber.*, 1900, 33, 494—499).—When an aqueous solution of citradibromopyrotartaric acid (1 mol.) is warmed on the water-bath with phenylhydrazine (3 mols.), carbon dioxide is evolved, and a deposit of Knorr's 1-phenyl-3-methylpyrazolone-4-azobenzene (Abstr., 1887, 602) and 1-phenyl-4-methyl-5-pyrazolone is formed; the two may be separated by the aid of benzene, in which the azo-derivative is soluble. The same phenylmethylpyrazolone is obtained when Wislicenus and Arnold's 1-phenyl-4-methylpyrazolone-3-carboxylic acid (*Annalen*, 1888, 246, 331) is distilled under 9 mm. pressure, or when ethyl-β-bromo-α-methylacrylate is heated at 120—130° with phenylhydrazine. The latter synthesis indicates that bromomethylacrylic acid is probably an intermediate product in the preparation of the pyrazolone from citradibromopyro-

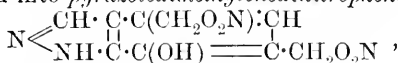
tartaric acid. 1-Phenyl-4-methyl-5-pyrazolone,  $NPh \begin{smallmatrix} \text{NH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{C}^{\text{Me}} \end{smallmatrix}$ , crystallises from alcohol in glistening, flat needles melting at 210°, and dissolves readily in both alkalis and acids, but does not react with nitrous acid, or yet with diazobenzene (Abstr., 1895, i, 395); with bromine, it yields a 4-bromo-1-phenyl-4-methyl-5-pyrazolone melting at 242°, and with benzaldehyde a benzylidene derivative melting and decomposing at 216—225°.

In the synthesis of 1-phenyl-4-methyl-5-pyrazolone from ethyl bromomethylacrylate, an isomeric base, 1-phenyl-4-methyl-3-pyrazolone, is always formed; in fact, it is the main product when the condensation takes place on the water-bath; it crystallises in glistening needles melting at 145°, yields a nitro-derivative which crystallises in yellow, glistening needles melting at 124°, an acetyl derivative, 2-acetyl-1-phenyl-4-methyl-3-pyrazolone, melting at 167°, and also reacts with diazobenzene. J. J. S.

Action of Diazomethane on Picryl Acetate. By HANS VON PECHMANN (*Ber.*, 1900, 33, 627—631. Compare Heinke, *Abstr.*, 1898, i, 413).—*Pyrazolinedimethylenepicryl acetate*,



and *trimethylenepicryl acetate*,  $\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{C}(\text{CH}_2\text{O}_2\text{N}) \cdot \text{CH} \\ \diagdown \\ \text{C}(\text{NO}_2) \cdot \text{C}(\text{OAc}) \cdot \text{C} \cdot \text{CH}_2\text{O}_2\text{N} \end{array}$ , are both obtained when powdered picryl acetate is added to an ethereal solution of diazomethane, and may be separated by careful treatment with cold acetone and water, in which the pyrazole derivative is the less soluble. Pyrazolinedimethylenepicryl acetate forms pale yellow, six-sided prisms melting and decomposing at  $144^\circ$ , is only sparingly soluble in alcohol, ether, or benzene, and when warmed with concentrated hydrochloric acid, or, still better, with alcohol and hydrochloric acid, is converted into *pyrazolinedimethylenedinitrophenol*,



which crystallises from acetic acid in colourless prisms melting at  $239.5^\circ$ , and when oxidised with nitric acid yields pyrazole-4:5-dicarboxylic acid (*Abstr.*, 1899, i, 948). Trimethylenepicryl acetate crystallises from dilute acetone or alcohol in colourless needles melting at  $140\text{--}141^\circ$ ; it dissolves readily in the usual solvents, and when warmed with dilute sulphuric acid, yields hydroxylamine. The constitution of the group  $\text{CH}_2\text{O}_2\text{N}$  is not known. J. J. S.

Diaminodixenylamine. By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1900, [ii], 61, 103—107).—*Diaminodixenylamine* [*di-p-amino-di-diphenylamine*],  $\text{NH}(\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$ , prepared by heating a mixture of benzidine and finely-divided benzidine hydrochloride in a current of carbon dioxide at  $330\text{--}340^\circ$ , distils at  $370\text{--}380^\circ$  under 2.5 mm. pressure, dissolves readily in hot aniline, and crystallises from a large volume of benzene in minute, white flakes; it blackens when heated in the air, but when heated in a sealed tube melts at  $220\text{--}221^\circ$ ; it forms a *hydrochloride*,  $\text{C}_{24}\text{H}_{21}\text{N}_3 \cdot 2\text{HCl}$ .

T. M. L.

Glauconic Acids. II. By OSCAR G. DOEBNER (*Ber.*, 1900, 33, 677—680. Compare *Abstr.*, 1898, i, 384).—Glauconic acids have been prepared from *p*-toluidine and *p*-anisidine; the methods were those employed previously, except that it was found best to oxidise the hydroglauconic to the glauconic acid by means of a concentrated solution of potassium ferrieyanide, avoiding an excess.

From *p*-toluidine: *Hydro-6-methylglauconic acid* melts at  $272^\circ$ ; *dihydro-6-methylquinaldine*, also obtained by distilling 6-methylquinaldine with zinc dust, smells like aniseed, boils at  $262\text{--}264^\circ$ , and forms a *picrate* melting at  $153^\circ$ ; *6-methylglauconic acid* forms dark blue flocks and yields alkali salts, crystallising in slender, blue needles.

From *p*-anisidine: *6-Methoxyhydroglauconic acid* is brownish-yellow, and melts and decomposes at  $228\text{--}230^\circ$ ; *6-methoxyglauconic acid* forms dark blue flocks; its alkali salts crystallise in blue needles with a

coppery lustre and dissolve in water and alcohol with a bluish-red fluorescence.

C. F. B.

**Action of Tetramethyldiaminobenzophenone on  $\alpha$ -Dinaphthylbenzidine.** By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1900, [ii], 61, 107—109).— $\alpha$ -Naphthylbenzidine condenses with 1 mol. only of tetramethyldiaminobenzophenone when the mixture reacts in naphthalene solution with phosphorus oxychloride; the product is a dark copper-coloured pigment with a metallic lustre, and is regarded as having the constitution



it was not isolated in a pure state.

T. M. L.

**Dihydro-1:2:3:4-tetrazine (Osotetrazine).** By HANS VON PECHMANN and WILHELM BAUER (*Ber.*, 1900, 33, 644—646).—*Dibenzoyldimethylsosotetrazine*,  $\begin{array}{c} \text{CMe:N}\cdot\text{NBz} \\ | \\ \text{CMe:N}\cdot\text{NBz} \end{array}$ , obtained by oxidising diacetyldi-

benzoylosazone, crystallises in white needles melting at 140°. On removing the benzoyl groups by means of hydrochloric acid, first *benzoyldimethylsosotetrazine*, forming white, nodular crystals melting at 95°, is obtained, and finally *dimethylsosotetrazine*,  $\text{C}_4\text{H}_8\text{N}_4$ , which crystallises, on adding light petroleum to its benzene solution, in colourless leaflets which melt at 95° and explode when quickly heated. Dimethylsosotetrazine is soluble in most solvents, its aqueous solution having a neutral reaction. With mercuric chloride, it gives a white precipitate, which crystallises from hot water in needles melting at 146—147°. Ferric chloride colours the solution yellowish-red, whilst on adding silver nitrate, colourless needles are slowly deposited. On boiling, it reduces Fehling's solution and alkaline silver solutions, and, when acted on by sulphuric acid and dichromate, undergoes vigorous oxidation, even in the cold.

T. H. P.

**Conversion of Tetrazine into Triazole Derivatives.** By MAX BUSCH and CARL HEINRICH (*Ber.*, 1900, 33, 455—463. Compare Hantzsch and Silberrad, this vol., i, 261).—*Diethyl diphenylcarbazide-dicarboxylate*,  $\text{CO}(\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$ , prepared by the action of carbonyl chloride on ethyl phenylcarbazinate, crystallises from light petroleum in white needles and melts at 194°.

*Phenylurazine*,  $\text{CO} \begin{array}{c} \text{NPh}\cdot\text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \text{---} \text{N} \end{array} \text{C}\cdot\text{OH}$ , prepared by the action of carbethoxyphenylhydrazinecarboxylic chloride,  $\text{COCl}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , on hydrazine hydrate, crystallises from water in large needles, and from alcohol in glistening flakes, melts at 244—245°, dissolves readily in alkali hydroxides or carbonates, has no basic properties, is not attacked by ferric chloride or mercuric oxide, and gives no definite oxidation product with potassium permanganate or with nitric acid; the *potassium* and *sodium* salts crystallise in glistening needles; the *triacetyl* derivative crystallises from alcohol in beautiful, colourless flakes and melts at 128°. With benzaldehyde, phenylurazine forms an

*additive* compound,  $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{N} \\ | \quad \diagup \quad \diagdown \\ \text{NPh}\cdot\text{CO}\cdot\text{N} \end{array} \text{C}\cdot\text{HPh}$ , or  $\text{N} \begin{array}{c} \text{CO}\cdot\text{NPh} \\ \diagdown \quad \diagup \\ \text{---CHPh---} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{C}(\text{OH}) \end{array} \text{N}$ , which



crystallises from alcohol in glistening flakes, melts at  $175^{\circ}$ , dissolves in dilute sodium hydroxide, and is decomposed by dilute acids. The *methyl ether* crystallises from alcohol, benzene, or water, melts at  $135\text{--}136^{\circ}$ , is readily decomposed by alkalis, and has no basic properties. By the action of nitrous acid, phenylurazine is converted into phenylurazole,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OH} \\ \diagup \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$  (Pinner, Abstr., 1887, 1043); the methyl ether similarly gives a *methyl phenylurazole*, to which the formula  $\text{NPh} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OMe} \\ \diagup \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$  or  $\text{NPh} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OMe} \\ \diagup \\ \text{C}(\text{OH})\cdot\text{N} \end{smallmatrix}$  is assigned; this crystallises from water in snow-white, glistening flakes, melts at  $182\text{--}185^{\circ}$ , and, unlike methylurazine, has acid properties, and dissolves in alkali carbonates. T. M. L.

**Diazotisation of Safranine.** By GEORGE F. JAUBERT (*Compt. rend.*, 1900, 130, 661—663).—The red, or monoacid, and the blue, or diacid, salts of phenosafranine are shown by titration with sodium nitrite solution to yield only monodiazio-derivatives; they therefore contain a single amino-group capable of diazotisation and possess a paraquinonoid structure. On the other hand, the green, or triacid, salts, which are stable only in concentrated acid solution, react with twice the quantity of sodium nitrite to form a bisdiazio-derivative, and have therefore the orthoquinonoid structure of an azonium base. N. L.

**Oxidation of Hydrazobenzene in Alkaline Alcoholic Solution by Atmospheric Oxygen.** By AUGUSTIN BISTRZYCKI (*Ber.*, 1900, 33, 476. Compare Bamberger, this vol., i, 220).—The oxidation of hydrazobenzene by atmospheric oxygen is greatly facilitated by adding alkali to the alcoholic solution. T. M. L.

**Transformation of Bromodiazonium Chlorides into Chlorodiazonium Bromides.** By ARTHUR HANTZSCH and J. S. SMYTHE (*Ber.*, 1900, 33, 505—522).—It is shown that certain *o*-bromodiazonium chlorides are readily transformed, either in the dry state or in solution, into *o*-chlorodiazonium bromides, by an intramolecular change. A similar, but slower, interchange also occurs when the halogen atoms are in the para-position relatively to one another, but no such change takes place between groups in the meta-position; thus 2:6-dibromobenzenediazonium chloride is more rapidly transformed than the 2:4-dibromo-compound, and 3:5-dibromotoluene-4-diazonium chloride than 3:5-dibromotoluene-2-diazonium chloride. Moreover, in the case of 2:4-dibromodiazonium chloride ( $\text{N}_2\text{Cl} = 1$ ) there is formed a greater proportion of 1-chloro-4-bromo- than of 4-chloro-1-bromo-diazonium bromide. Experiments with 2:4:6-tribromodiazonium chloride show that the rate of transformation in solution is apparently inversely proportional to the dissociating power of the solvent; thus it is most rapid in ethyl alcohol, less so in glacial acetic acid, still less in methyl alcohol, and is almost zero in aqueous solution. Experiments with the same salt in methyl alcoholic solution show that the transformation occurs according to the equation  $k = 1/t \cdot \log. a/a-x$  characteristic of a unimolecular reaction; this, taken in conjunction with the inhibiting

action of dissociating solvents, proves that the change is *intra*- and not *inter*-molecular.

By increasing the number of bromine atoms in the benzene nucleus, the rate of interchange of chlorine and bromine is greatly accelerated; thus both *o*- and *p*-bromodiazonium chlorides remain unchanged in alcoholic solution, although 2:4- and 2:6-dibromobenzenediazonium chlorides and 3:5-dibromotoluene-2- and -4-diazonium chlorides are rapidly transformed. With 2:4:6-tribromobenzene- and 2:4:6-tribromotoluene-3-diazonium chlorides, the action is still more rapid, whilst all attempts to prepare pentabromobenzenediazonium chloride free from the isomeric bromide formed by transformation were fruitless. On diazotising pentabromoaniline hydrochloride in ethereal solution and subsequently boiling with alcohol, 2:4:6-trichlorodibromobenzene (m. p. 119°) is formed.

A methyl group in the ortho- or para-, or even in the meta-position relatively to the diazo-group diminishes the tendency towards interchange between chlorine and bromine; increasing the dilution has the same effect, whilst raising the temperature greatly accelerates the transformation. In aqueous solution, the rate of transformation is increased by increasing the number of free halogen ions, or more markedly by increasing the number of hydrogen ions.

The diazo-salts of pentabromoaniline can be isolated only with difficulty; the *diazo-nitrate* is described, but attempts to prepare the diazo-bromide yielded only the *perbromide*,  $C_6Br_5 \cdot N_2 \cdot Br_3$ , as a crystalline powder exploding at 170°; this perbromide, when boiled with alcohol, yields hexabromobenzene, and treatment with aqueous ammonia gives rise to *pentabromodiazobenzeneimide*,  $C_6Br_5 \cdot N_3$ , which decomposes at about 155°.

W. A. D.

**Cause of Ehrlich's Diazo-reaction [in Urine].** By LUDWIG BRIEGER (*Chem. Centr.*, 1900, i, 373; from *Med. Woch.*, 1900, 6).—The author has attempted to isolate the substance which causes the diazo-reaction. Urine from patients suffering from phthisis and typhoid was precipitated with lead acetate, and the precipitate decomposed by means of hydrogen sulphide. The filtrate was then evaporated in a vacuum to a syrup which gave a strong diazo-reaction. The phosphates were removed by means of ammonia and alcohol, and the filtrate evaporated; the residue was dissolved in water and the filtrate yielded with alcohol a deliquescent precipitate which showed the diazo-reaction in a high degree. It is non-poisonous. The author has not as yet succeeded in obtaining a perfectly pure product (compare Clemens, this vol., i, 227).

L. DE K.

**A Cuprous Salt of Diazoaminobenzene.** By LOUIS MEUNIER and A. RIGOT (*Bull. Soc. Chim.*, 1900, [iii], 23, 103—106).—When a concentrated alcoholic solution of diazoaminobenzene is agitated for about 12 hours with freshly prepared powdered copper, and the product washed with alcohol and finally exhausted with boiling benzene, a compound,  $Cu_2(NPh \cdot N:NPh)$ , is obtained which crystallises in orange-yellow needles, decomposes at 270°, and is insoluble in water, alcohol, ether, or light petroleum. When treated with hydrogen sulphide in benzene solution, it is decomposed, with production of

cuprous sulphide and diazoaminobenzene; it is also decomposed by dilute acetic and hydrochloric acids, with the liberation of two-thirds of the nitrogen, and by nitric acid with explosion and incandescence. If, however, dry hydrogen chloride is passed into the benzene solution of the compound, an unstable, yellowish-white substance, of the composition  $\text{Cu}_2(\text{NPhHCl}\cdot\text{N}\cdot\text{NPh})$ , is precipitated; this is soluble in water.

Sodium diazoaminobenzenedi-*p*-disulphonate reacts with powdered copper to form an amorphous, orange-yellow compound which is soluble in water, and is decomposed by hydrogen sulphide and by dilute acetic acid. A similar substance, for which no solvent could be found, appears to be formed from *p*-dinitrodiazoaminobenzene.

N. L.

**The Condition of Nitrogen in the Proteid Molecule.** By WALTHER HAUSMANN (*Zeit. physiol. Chem.*, 1900, 29, 136—145. Compare Abstr., 1899, i, 653).—A number of other proteids have now been subjected to analyses on the plan previously adopted. The following table gives the main results:—

Proteid.	Amidic nitrogen, per cent.	Diamino- nitrogen, per cent.	Monamino- nitrogen, per cent.
Casein .....	13·37	11·71	75·98
Crystallised egg albumin .....	8·53	21·33	67·80
Oxyhaemoglobin (horse).....	6·18	23·51	63·26
Serum-globulin (horse).....	8·9	24·95	68·28
Proto-albumose (from fibrin)..	7·14	25·42	68·17
Globin (horse) .....	4·62	29·37	67·08
Proteids of pine seeds .....	10·3	32·8	56·90
Gelatin .....	1·61	35·83	62·56
Edestin .....	10·25	38·15	54·99
Hetero-albumose (from fibrin)	6·45	38·93	57·40

W. D. H.

**Proportion of Basic Nitrogen in Elastin.** By ALLAN C. EUSTIS (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xxxi).—The proportion of basic nitrogen split off from elastin by hydrochloric acid is differently given by different observers. Five experiments are here recorded, and the results vary from 0·86 to 17·69 per cent.

The conclusion is drawn that the method in use for the separation of hexon bases by phosphotungstic acid is untrustworthy quantitatively.

W. D. H.

**Mucin from Bone.** By WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, vii—viii).—After the removal of the inorganic substances from bone, lime-water extracts from the residue a mucin-like substance. Young formerly failed to obtain mucin; he did not, however, first remove the inorganic substances (Abstr., 1893, ii, 134).

W. D. H.

**Mucin.** By P. A. LEVENE (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, viii).—The acid properties of mucins are not

explained on the general supposition that a mucin is a compound of proteid and carbohydrate. Both tendon mucin and submaxillary mucin yield an acid substance on decomposition. It contains sulphur, and preliminary experiments indicate it to be a substance similar to chondroitin-sulphuric acid, in which the sulphuric acid is in ethereal combination.

W. D. H.

**Basic Decomposition Products of Edestin.** By P. A. LEVENE and LAFAYETTE B. MENDEL (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, iv).—Pure crystallised edestin was decomposed by hydrochloric acid and stannous chloride. In the phosphotungstic acid precipitate, the bases histidine, lysine, and arginine were separated by Kossel's method.

W. D. H.

**Ovarial Mucoids.** By J. B. LEATHES (*Chem. Centr.*, 1900, i, 45; from *Arch. exp. Path. Pharm.*, 43, 245—258).—*Paramucosin*,  $C_{12}H_{22}O_{10}N$ , probably  $OH \cdot CH_2[CH(OH)]_4 \cdot CH:N \cdot CH(CHO) \cdot [CH(OH)]_3 \cdot CH_2 \cdot OH$ , obtained from Mitjukoff's paramucin (*Arch. Gynäk.*, 49, 278) by means of the copper alkali method, possesses reducing properties and when decomposed by hydrochloric acid yields a simple osamine and not a glucosamine. By boiling the impure paramucosin, from which the albumin has been removed, with potassium hydroxide solution, a base is formed which may be easily separated from paramucosin by boiling the copper compound. Like protamine, this base gives the biuret reaction. It is precipitated by phosphotungstic acid, but not by ferrocyanic or nitric acid and does not give Millon's reaction.

E. W. W.

**Cyano-methæmoglobin and Photo-methæmoglobin.** By JOHN SCOTT HALDANE (*J. Physiol.*, 1900, 25, 230—232).—Bock (*Skand. Arch. Physiol.*, 6, 299) prepared, by the influence of light on methæmoglobin crystals, a red substance giving a spectrum very much like that of hæmoglobin; it is crystallisable and he termed it photo-methæmoglobin. Kobert (*Maly's Jahresb.*, 1891, 443) found that when hydrocyanic acid or a cyanide is added to a solution of methæmoglobin, a similar red colour is obtained; this may be used as a delicate test for hydrocyanic acid. The present research shows the two substances are identical; the action of light is to liberate hydrocyanic acid from the potassium ferrieyanide used to prepare methæmoglobin. Cyano-methæmoglobin is doubtless a cyanogen compound of hæmoglobin, but there is no displacement of oxygen. It is not identical with Hoppe-Seyler's cyanhæmatin as stated by Szigeti (*Maly's Jahresb.*, 1893, 620).

W. D. H.

**Neutral Hæmatin.** By V. ARNOLD (*Zeit. physiol. Chem.*, 1900, 29, 78—85).—Neutral hæmatin, which has not been described before, is of a yellowish-red colour; the yellow tint, as in oxyhæmoglobin, being more pronounced on dilution. It shows two absorption bands rather nearer the violet end of the spectrum than those of oxyhæmoglobin. It can be obtained from oxyhæmoglobin or more readily from methæmoglobin solution by adding sodium chloride and then from a third to a half the volume of alcohol; the presence of the salt prevents precipitation by the alcohol. It may also be obtained

by neutralising a solution of alkaline hæmatin, and dissolving out with alcohol in the presence of salt; dilution with water precipitates it. By heat, the red colour is changed to brown, and the spectrum of alkaline hæmatin is seen; the colour and absorption bands of neutral hæmatin return on cooling.

W. D. H.

**Decomposition Products of Hæmatin.** By WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1900, 29, 185—192. Compare Abstr., 1899, i, 468, and this vol., i, 68).—It appeared probable in former work that the substance  $C_8H_8O_5$  was not a primary oxidation product of hæmatin, but was due to secondary changes [occurring in the dibasic hæmatic acid,  $C_8H_9NO_4$ ]. This view is now confirmed by further experiments.

W. D. H.

**Preparation of *a*- and *b*-Nucleic Acid, and of Nucleothymic Acid.** By ALBERT NEUMANN (*Chem. Centr.*, 1899, ii, 1028; from *Arch. Anat. Phys.*, 1899, 552—555. Compare Abstr., 1899, i, 467).—Prepared thymoid glands, after boiling with very dilute acetic acid, are macerated and then boiled with a solution of sodium acetate containing a little sodium hydroxide, the boiling being continued for half an hour if the *a*-acid is required, and for 2 hours for the *b*-acid. After neutralising with dilute acetic acid, the liquid is filtered hot, evaporated at  $40^\circ$  to  $\frac{1}{2}$ —1 litre, and then treated with an equal volume of alcohol, when the sodium salt separates on cooling. Nucleothymic acid is prepared by dissolving *a*- or *b*-nucleic acid in 20 times its weight of water at  $60^\circ$  as quickly as possible, and pouring the solution into 3 times its volume of alcohol containing 15 c.c. of concentrated hydrochloric acid per litre. The precipitate is dissolved in cold water and again precipitated by alcoholic hydrochloric acid solution.

E. W. W.

**Thymin.** By WALTER JONES (*Zeit. physiol. Chem.*, 1900, 29, 20—23).—Thymin was originally described by Kossel as one of the decomposition products of the nucleic acid of the thymus gland. It has since been obtained from nucleic acid from other sources. Its constitution is not known, although its low percentage of hydrogen possibly indicates a cyclic structure. *Bromothymin*,  $C_5H_7O_2N_2Br$ , crystallises in long, concentrically-grouped, transparent prisms, and begins to decompose at  $130^\circ$ . Thymin is isomeric, not identical, with methyluracil.

W. D. H.

**Reactions of Phrenosin, the Cerebro-galactoside from the Human Brain.** By JOHN L. W. THUDICHUM (*J. pr. Chem.*, 1899, [ii], 60, 487—506. Compare Abstr., 1882, 537, and 1896, i, 400).—When phrenosin is triturated with a concentrated aqueous solution of mercuric nitrate, and the product dissolved in strong nitric acid and reprecipitated by the addition of water, a compound is obtained which contains no mercury; it is soluble in ether, and on evaporation of the ethereal solution remains as a hard, snow-white mass, which, on treatment with water, swells and gradually becomes transparent.

A hot alcoholic solution of phrenosin yields with strong aqueous mercuric nitrate, a thick, white precipitate, in which  $N : Hg = 3 : 4$ . If this substance is washed with dilute nitric acid, a white residue is

obtained of the composition  $C_{41}H_{79}O_8N, 2HgNO_3, 3HgO, 2H_2O$ , which is insoluble in alcohol, ether, or benzene; when heated at  $85-100^\circ$  in a stream of dry air, it loses water, becomes yellow, and is then soluble in ether.

Sphingosine (Abstr., 1882, 537) melts at  $75-80^\circ$ , and resolidifies at  $70^\circ$ . It yields the oleocholide reaction in the presence of sucrose. The *nitrate*,  $C_{17}H_{35}O_2N, HNO_3$ , is a white, crystalline salt, which reacts with mercuric nitrate to form the compounds  $C_{17}H_{35}O_2N, HgNO_3$  and  $C_{17}H_{35}O_2N, HgO$ ; on heating the latter with nitric acid, an acid, probably isomeric with palmitic acid, is formed; the *picrate* melts at  $75^\circ$ ; the *platinichloride* forms slender needles. A double platinichloride of sphingosine and psychosine,

$C_{17}H_{35}O_2N, HCl, C_{33}H_{45}O_7N, PtCl_4$ ,  
crystallises from alcohol in slender needles.

When hydrolysed with baryta, *sphingomyelin*,  $C_{58}H_{121}O_{10}N_2P$ , does not yield glycerophosphoric acid, but neurine and a "phosphatide" which contains the sphingosyl radicle, are produced. Sphingomyelin reacts with cadmium chloride to form the compound



The paper concludes with a complete list of the products which the author has obtained from phrenosin. E. G.

**Seminase, a new Enzyme.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 130, 340—342. Compare this vol., ii, 35).—The enzyme obtained from the seeds of fennugreek and lucerne rapidly hydrolyses the albumen obtained from carob-tree, but only slowly hydrolyses potato-starch. A parallel experiment made with diastase gave very slow hydrolysis in the former and rapid hydrolysis in the latter case. To this enzyme, which is present in considerable amount in the above seeds, the name *seminase* is given. H. R. LE S.

**Precipitation of Zymase from Yeast Extract.** By ROBERT ALBERT and EDUARD BUCHNER (*Ber.*, 1900, 33, 266—271).—On pouring yeast extract into twelve times its volume of absolute alcohol or, better, into a mixture of 10 vols. of alcohol and 2 vols. of ether, a flocculent precipitate is obtained containing nearly the whole of the zymase, the activity of the latter not being impaired by drying; with less alcohol, the precipitation is not complete. It appears that the active zymase only constitutes a very small percentage by weight of the precipitate, and redissolves only slowly on stirring with water, having apparently undergone some change under the influence of the alcohol; several hours contact with alcohol diminishes the activity of zymase in a very marked manner. Acetone only partially precipitates zymase from yeast extract. W. A. D.

## Organic Chemistry.

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**Certain Laws and their Application in Organic Chemistry.** By ARTHUR MICHAEL (*J. pr. Chem.*, 1899, [ii], 60, 286—384; 409—486. Compare Abstr., 1888, 1055, 1056).—An attempt is made to account for various reactions, chiefly of organic compounds, from a single point of view, by considering the sum of the influences exerted upon one another, directly and indirectly, by all the atoms in the molecule. The reactions considered are for the most part the addition and elimination of halogens, hydrogen haloids, and water; and the substitution of halogens for hydrogen, and of hydroxyl for halogens and *vice versa*. Several reactions have been reinvestigated by improved methods; namely, the polymerisation of allylene under the influence of sulphuric acid, and the addition of hydrogen iodide, bromine chloride, iodine chloride, and hypochlorous acid to propylene. It was found that a single additive product is seldom, if ever, formed; the other possible isomeride is also formed, although often in a very small amount. An ingenious method of separating isomeric ketones (into which isomeric halogen derivatives can be converted, through the carbinols) by means of their different behaviour with semicarbazide salts is described. With the dichloroacetate, for instance, 2-pentenone forms a semicarbazone, but 3-pentenone does not; the latter does, however, with semicarbazide hydrogen phosphate, and so does 2-hexenone, but not 3-hexenone.

The paper is not one that admits of satisfactory abstraction; reference must be made to the original. C. F. B.

**Preparation of Saturated Hydrocarbons.** By ALESEI A. WOLKOFF and BORIS N. MESSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1009—1015).—The gases of the paraffin series are readily prepared by adding alcohol (1 mol.), drop by drop, to a mixture of an alkyl iodide (1 mol.) and twice the calculated quantity of powdered magnesium, no extraneous heating being required. This method of preparation, although furnishing a good lecture experiment, yields hydrocarbons containing appreciable quantities of free hydrogen, the proportion of which is largely increased if the alcohol is used in excess; traces of the alkyl iodide are also present, even after the gas has been passed through a reflux condenser, but are removed by washing with alcohol. Better results are obtained by warming in a water-bath a mixture of equal parts of zinc dust and alkyl iodide, together with a quantity of water equivalent to the iodide taken; the reaction, which should be carried out in a flask connected with a reflux condenser, begins at 50—60° and is completed at 100°. Thus prepared, the gases contain no free hydrogen, but a small quantity of unsaturated compounds which are entirely removed by means of potassium permanganate either in solution or in the moist state.

T. H. P.

**Velocity of Formation of Olefines.** By S. BRUSSOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 7—28).—A series of experiments has been carried out on the action of alcoholic alkali solutions on alkyl halogen compounds. The alkyl haloid, together with an equivalent quantity of alcoholic potash, was heated in a bath of benzene vapour and the olefine collected in a graduated tube over water; the time taken for each 20 c.c. of gas to collect is regarded as the velocity of the reaction during that time. The proportion of the ether formed along with the olefine is obtained by determining the amount of potash left undecomposed at the end of the reaction. From a preliminary experiment with *isobutyl* iodide, it was found that the curve plotted with the velocities of reaction as ordinates and the total amount of reaction, as measured by the volume of gas evolved, as abscissæ, is not regular unless a certain quantity of potassium iodide is added; this was therefore done in all the following experiments. The curves thus obtained for propyl, *isopropyl*, butyl, *isobutyl*, *sec*-butyl, and *tert*-butyl iodides, and for *isopropyl* and *isobutyl* bromides, rise quickly to a maximum, then fall and finally become straight lines, which theory would indicate them to be. Further, the theoretical maxima of the curves, namely, the points where the rectilinear parts meet the vertical axis, are very nearly identical with the observed maximum velocities of reaction. In the case of *tert*-butyl iodide, considerable deviation from this behaviour occurs, as after rising to a maximum the velocity of reaction remains constant for some time and then falls regularly.

The different alkyl iodides yield very different proportions of olefines; thus, using quantities of the iodides capable of giving 300 c.c. of olefine, the following are the actual volumes obtained: from ethyl iodide, 54 c.c.; propyl iodide, 122 c.c.; *n*-butyl iodide, 117 c.c.; *tert*-butyl iodide, 245 c.c.; *isobutyl* iodide, 265 c.c.; *isopropyl* iodide, 278 c.c.; *sec*-butyl iodide, 290 c.c. Thus the yield of olefine is least with normal iodides and is increased by lengthening the carbon atom chain and also by introducing side-chains. The maximum velocities of reaction for the four butyl iodides have the following relative values: for the normal compound, 1; the *iso*-compound, 2·84; the secondary, 5·06; and the tertiary, 8·00. Hence the velocity of reaction has also its least value for a normal carbon chain and is greater, the greater the number of side-chains present in the molecule; it is further increased if the iodine atom and a side-chain are joined to the same carbon atom. A comparison of the volumes of olefine obtained and of the maximum velocities of reaction when different halogen compounds of the same alkyl group are employed shows that the iodo-compounds are much more suitable than the bromides for the preparation of olefines, whilst the chlorides are quite unsuitable. The replacement of ethyl by methyl alcohol as a solvent makes no difference either in the volume of olefine obtained or in the velocity of reaction in the cases of *iso*- and *sec*-butyl iodides; with the *tert*-iodide, although the same volume of olefine is obtained, yet the maximum velocity of reaction when methyl alcohol is employed is 2·5 times as great as with ethyl alcohol. The use of alcoholic soda instead of potash makes little difference to the volume of gas or to the velocity of reaction.

T. H. P.



**Laboratory Method for the Continuous and Uniform Generation of Acetylene, and for its Purification.** By JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1900, 22, 106—108).—Acetylene is evolved in a steady stream when calcium carbide is covered with absolute alcohol, and water added drop by drop. It may be purified by passing it through a solution of copper sulphate acidified with sulphuric acid, and afterwards over pumice stone saturated with an acetic or sulphuric acid solution of chromic acid.

E. G.

**Gold Carbide.** By JOHN A. MATHEWS and L. L. WATERS (*J. Amer. Chem. Soc.*, 1900, 22, 108—111).—The yellow explosive precipitate, which Berthelot (*Ann. Chim. Phys.*, 1866, [iv], 9, 425) found to be produced when acetylene is passed into a solution of aurous thiosulphate, is *aurous carbide*,  $\text{Au}_2\text{C}_2$ . It is decomposed by hydrochloric acid with the formation of acetylene and aurous chloride, and on boiling with water is resolved into its constituent elements.

By the action of acetylene on solution of auric chloride, metallic gold is precipitated, but no precipitate is produced if the solution has been rendered alkaline with potassium hydroxide; solution of potassium auric cyanide also yields no precipitate.

E. G.

**Action of Amyl Chloride on Calcium Carbide.** By P. LEFEBVRE (*Compt. rend.*, 1900, 130, 1036—1039).—The liquid products of the action of amyl chloride on calcium carbide at a dull red heat include  $\beta$ -methyl- $\Delta^2$ -butylene,  $\beta$ -methyl- $\Delta^3$ -butylene, and *sec*-amyl and *tert*-amyl chlorides, whilst the gaseous products consist of hydrogen, acetylene, ethylene, and other hydrocarbons of the ethylene series. The primary reaction is considered to be  $\text{CaC}_2 + 2\text{C}_5\text{H}_{11}\text{Cl} = \text{C}_2\text{H}_2 + 2\text{C}_5\text{H}_{10} + \text{CaCl}_2$ . N. L.

**Compounds of Aluminium Haloid Salts with Organic and Inorganic Substances. II.** By MICHAEL I. KONOWALOFF and W. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1020—1027. Compare Abstr., 1899, i, 470).—The molecular weight of the compound  $(\text{AlBr}_3, \text{EtBr})_2, \text{CS}_2$  (*loc. cit.*) in boiling ethyl bromide, has for a 6 per cent. solution the value 940.4, and for a 20 per cent. solution 1778, the number required by the formula being 828.

Bromoform and aluminium bromide react in carbon disulphide solution with the formation of the *compound*,  $\text{AlBr}_3, \text{CHBr}_3, \text{CS}_2$ , which separates in slender, prismatic, yellow, dichroic crystals which, when heated out of contact with air, melt and partially decompose at  $120.7$ — $121.3^\circ$ ; it dissolves slightly in ethyl bromide and more readily in ether. In aqueous solution, it decomposes with the formation of aluminium hydroxide, hydrogen bromide, and *bromomethylene dithiocarbonate*,  $\text{CO} \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{CHBr}$ ; this compound separates from ether in hard, almost colourless crystals which are soluble in ether or light petroleum, and melt and decompose at  $52$ — $52.5^\circ$ .

Ethylidene bromide readily reacts with aluminium bromide in carbon disulphide solution, giving the *compound*  $\text{AlBr}_3, \text{C}_2\text{H}_4\text{Br}_2, \text{CS}_2$ , whilst from tribromopropene  $\text{AlBr}_3, \text{C}_3\text{H}_3\text{Br}_3, \text{CS}_2$  is obtained.

T. H. P.

**Iodide of Cuprous Acetylide.** By MARCELLIN P. E. BERTHELOT and MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1900, [vii], 19, 54—56).—The *iodide*,  $\text{Cu}_3\text{C}_2\text{I}\cdot\text{CuI}$ , of cuprous acetylide is obtained as a bright red precipitate by passing acetylene into a slightly alkaline solution of cuprous iodide in potassium iodide; the quantity of alkali present must not exceed the amount required to combine with the hydrogen iodide set free during the formation of cuprous acetylide, otherwise substances containing more copper, such as  $3\text{Cu}_2\text{C}_2$ ,  $\text{Cu}_2\text{I}_2$  and  $\text{Cu}_2\text{C}_2\cdot\text{Cu}_2\text{I}\cdot\text{OH}$ , are produced; the latter of these, when dehydrated, yields the compound  $(\text{Cu}_2\text{C}_2\cdot\text{Cu}_2\text{I})_2\text{O}$ . G. T. M.

**Nitration of Menthane and of Triethylmethane.** By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1027—1029).—[With A. JEBENKO.]—When menthane is heated at  $110^\circ$  with nitric acid of sp. gr. 1.075, a mixture of *mononitro* compounds,  $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N}$ , is obtained, about 71 per cent. of the product being tertiary nitro-compound and the rest primary and secondary. When heated with dilute nitric acid, menthane is partially converted into *diisobutyl* and *diisoamyl*.

[With S. KOTSINA.]—On nitrating triethylmethane at  $120^\circ$  with nitric acid of sp. gr. 1.075, 57 per cent. of the product consists of the *tert*-nitro-derivative, which boils at  $190$ — $191^\circ$  under 743 mm. pressure, and has a sp. gr. 0.9623 at  $0^\circ/0^\circ$  and 0.9471 at  $20^\circ/0^\circ$ ; its molecular refraction (Lorenz and Lorentz formula) is 39.437 at  $20^\circ$ . The remainder (43 per cent.) of the nitrated product, which is a mixture of the primary and secondary nitro-derivatives, boils at  $195$ — $197^\circ$  under 750 mm. pressure, has a sp. gr. 0.9603 at  $0^\circ/0^\circ$  and 0.9452 at  $20^\circ/0^\circ$ ; its molecular refraction (Lorenz and Lorentz formula) is 40.065.

T. H. P.

**Salts of Nitro-compounds with Nitrated Bases.** Separation of Nitro-compounds of Different Types. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 73—75).—The ammonium salts of primary or secondary nitro-compounds are readily obtained by the action of ammonium chloride on the corresponding sodium or potassium compounds. The other method of preparing these salts, namely, by the action of alcoholic ammonia on the nitro-compound, gives good results with *o*-nitrodiphenylmethane, *o*-nitrotoluene, and primary nitromesitylene and nitro-*p*-xylene; the reaction in these cases takes place with development of heat and proceeds to an end, the solid ammonium salt being obtained. With the primary fatty compounds, nitromethane, nitroethane, nitropentane, nitrodiisoamyl and nitromenthane, very slight action takes place with alcoholic ammonia, whilst no ammonium salt is produced with nitrohexamethylene or  $\beta$ -nitro- $\gamma$ -ethylpentane, which are secondary nitro-compounds. The action of alcoholic ammonia can hence be used as a method of separating nitro-compounds of different types, as the ammonium salts of these compounds are in general readily soluble in water, and therefore can be easily removed from any nitro-compound not acted on by the ammonia.

Another means of separation of different nitro-compounds is presented by piperidine, which reacts energetically with nitro-compounds

containing a phenyl group to form well-crystallised salts, whilst with other nitro-derivatives, piperidine reacts only slightly or not at all.

Aqueous solutions of the ammonium salts of nitro-compounds are decomposed on the water-bath, ammonia being evolved and the nitro-derivative left behind. On heating the ammonium salt of *o*-nitrodiphenylmethane at above 150°, water and gases are evolved and a nearly theoretical yield of benzophenone obtained; this may be useful as a general method of converting secondary nitro-compounds into ketones.

T. H. P.

**Pentahydric Alcohol from Methylallylcarbinol.** By STEPHAN MAXIMOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 61—65).—When methylallylcarbinol is oxidised by gradually adding 1 per cent. potassium permanganate solution, a *pentahydric alcohol* of the constitution  $\text{OH} \cdot \text{CMe}[\text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}]_2$  is obtained; it is a viscid liquid with a sweet taste, and dissolves in water or alcohol, but is almost insoluble in ether. With acetic anhydride, it gives a mixture of a *tetra-acetyl* derivative with a small quantity of the *penta*-compound, the difficulty in completely acetylating being due to the tertiary nature of one of the hydroxyl groups. The mixed acetyl derivative is a colourless, viscous liquid, soluble in water, alcohol, or ether.

T. H. P.

**Sulphine and Thetine Derivatives.** By DANIEL STRÖMHOLM (*Ber.*, 1900, 33, 823—841. Compare Abstr., 1898, i, 624; this vol., i, 12).—Trimethylsulphine iodide boils slightly above 200° without previously melting, the *picrate* melts at 193°, the *acid tartrate* and the *antimonyl tartrate*,  $\text{SMe}_3 \cdot \text{CO}_2 \cdot \text{C}_7\text{H}_4\text{O}_2 \cdot \text{CO}_2(\text{SbO}) + \frac{1}{2}\text{H}_2\text{O}$ , form deliquescent plates; the *stannochloride*,  $\text{SMe}_3\text{Cl} \cdot \text{SnCl}_2$ , melts and decomposes at 216°, and the *lead salt*,  $\text{SMe}_3\text{Cl} \cdot \text{PbCl}_2$ , crystallises in needles.

Ethyl isopropyl sulphide combines with methyl iodide, at the ordinary temperature, to form *methylethylisopropylsulphine iodide*,  $\text{SMeEtPr}^{\beta}\text{I}$ , a white, deliquescent substance; the *cadmioiodide*,  $2\text{C}_6\text{H}_{15}\text{IS} \cdot \text{CdI}_2$ , melts at 166°, and the *platinichloride*,  $(\text{SMeEtPr}^{\beta})_2 \cdot \text{PtCl}_6$ , forms large, reddish-yellow, orthorhombic crystals, and on heating at 140° loses isopropyl chloride yielding the *compound*,  $(\text{SMeEt})_2 \cdot \text{PtCl}_4$ , which melts at 163°. The *stannichloride*,  $(\text{C}_6\text{H}_{15}\text{S})_2 \cdot \text{SnCl}_6$ , forms well-defined crystals, and melts and decomposes at 190°.

*Methylethylpropylsulphine iodide*,  $\text{SMeEtPr}^{\alpha}\text{I}$ , is non crystalline, but yields a *platinichloride* which forms reddish-yellow, monoclinic crystals [ $a : b : c = 1.733 : 1 : 1.712$ ;  $\beta = 81^\circ 54'$ ], and decomposes at 140°, without yielding a compound analogous with that derived from the corresponding isopropyl derivative; the *stannichloride* forms lustrous crystals and melts at 220°.

Methylethylbutylsulphine *platinichloride* forms ill-defined crystals; the corresponding *isobutyl* derivative,  $(\text{C}_7\text{H}_{17}\text{S})_2 \cdot \text{PtCl}_6$ , forms lustrous, reddish-brown, monoclinic crystals [ $a : b : c = 1.0230 : 1 : 0.8880$ ,  $\beta = 83^\circ 38'$ ], and the analogous *sec-butyl* compound regular octahedra. Methylethylamylsulphine *platinichloride* forms long prisms, whilst

methylethylhexylsulphine *platinichloride* melts at  $124^{\circ}$ ; the *platinichlorides* of methylethylsecocetyl sulphine, methyl dipropyl sulphine, methyl diisopropyl sulphine [rhombic crystals,  $a:b:c = 1.3500:1:1.3794$ ], methyl propylisobutyl sulphine, methyl isopropylisobutyl sulphine, methyl diisobutyl sulphine, and methyl diamyl sulphine are also described.

In the interaction of benzyl ethyl sulphide with methyl iodide, partial rearrangement occurs, dimethylethyl sulphine iodide being formed as well as benzyl methyl sulphine iodide; the *platinichloride* derived from the latter forms small, reddish-yellow needles and melts at  $142-144^{\circ}$ . Benzyl methyl isopropyl sulphine *platinichloride* forms sparingly soluble plates and melts at  $160^{\circ}$ .

A table of solubilities of all the *platinichlorides* described is appended.

The *bromide*,  $\text{O:S} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SMeBr}$ , forms white, easily soluble crystals, and melts and decomposes at  $181-184^{\circ}$ ; the *platinichloride*,  $(\text{C}_5\text{H}_{11}\text{OS}_2)_2\text{PtCl}_6$ , derived therefrom was also prepared. The action of chlorine on oxydiethylenedisulphidemethyl sulphine chloride yields the *dichloro*-derivative,  $\text{C}_5\text{H}_9\text{OS}_2\text{Cl}_2$ , which forms sparingly soluble crystals and decomposes at  $167^{\circ}$ ; the *monochloro*-derivative,  $\text{C}_5\text{H}_{10}\text{OS}_2\text{Cl}_2$ , is obtained with greater difficulty, and decomposes at  $140^{\circ}$ .

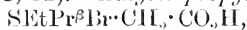
Thetine bromide and bromoacetic acid do not interact in aqueous solution; in the dry state, they yield at  $100^{\circ}$  a brown, semi-liquid product, insoluble in water. Similar indefinite results were obtained with methyl iodide and thetine bromide, and with bromoacetic acid and diethylenedisulphidemethyl sulphine iodide.

*Dimethylacetaldyl sulphine iodide*,  $\text{SMe}_2\text{I} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$ , cannot be obtained by the interaction of dimethyl sulphide with chloroacetal, but is prepared from methylthioacetal,  $\text{SMe} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$ , and methyl iodide; it forms slender, silky crystals, and the *platinichloride*, small, yellow, monoclinic plates [ $a:b:c = 1.3110:1:1.6618$ ;  $\beta = 72^{\circ}50'$ ].

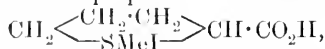
*Methylethylacetaldyl sulphine platinichloride*,  
 $[\text{SMeEt} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2]\text{PtCl}_6$ ,  
 forms large, yellowish-red, monoclinic crystals

[ $a:b:c = 1.4438:1:1.6381$ ;  $\beta = 66^{\circ}29'$ ].

Methylethylthetine tartrate could not be obtained crystalline, and attempts to resolve the compound into optically active components by means of ferments and "other methods" failed (compare Pope and Peachey, *Proc.*, 1900, 16, 12). *Ethylisopropylthetine bromide*,



is a white powder, which does not yield a crystalline compound with cinchonine; *ethylisobutylthetine bromide* forms long, thin needles, and melts and decomposes at  $109^{\circ}$ ; *benzylethylthetine platinichloride*,  $(\text{C}_{11}\text{H}_{15}\text{O}_2\text{S})_2\text{PtCl}_6$ , was also prepared. The *iodide*,



prepared from tetrahydro-2-thiophencarboxylic acid and methyl iodide, is a white mass, whilst the *thetine*,  $\text{C}_6\text{H}_{10}\text{O}_2\text{S} + \text{H}_2\text{O}$ , obtained therefrom separates from alcohol in beautiful crystals, and melts at  $105^{\circ}$ ; the corresponding *bromide* forms large, rhombohedral crystals,

and melts at  $128^{\circ}$ ; the *aurichloride*,  $C_6H_{11}O_2SAuCl_4$ , decomposes at  $170^{\circ}$ , and the *platinichloride* forms triclinic crystals

$[a : b : c = 1.309 : 1 : 1.726 ; \alpha = 62^{\circ}33', \beta = 83^{\circ}24', \gamma = 80^{\circ}42']$ , and decomposes at  $190^{\circ}$ .

Vinyl bromide and dimethyl sulphide do not interact. *Ethyl vinyl sulphide*, prepared from ethylsodiummercaptan and vinyl bromide, boils at  $90.5-91.5^{\circ}$  (uncorr.), has a sp. gr. 0.887 at  $14^{\circ}$ , and does not react with methyl iodide at the ordinary temperature; at  $50^{\circ}$ , dimethyl-ethylsulphine appears to be formed rather than methylethylvinylsulphine.

None of the compounds described containing an asymmetric sulphur atom could be resolved into optically active components by means of *Penicillium glaucum*, or by means of the strychnine or tartaric acid salts; in most cases, the acid tartrates formed non-crystallisable syrups. The thetine salts of the type  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{SMeX} \end{smallmatrix} CO_2H$ , which should exist in *cis*- and *trans*-forms, were found to be perfectly homogeneous, whilst no transformation phenomenon was observed in dealing with them.

W. A. D.

**Attempts to obtain Optical Antipodes of Quadrivalent Sulphur Derivatives.** By L. VANZETTI (*Gazzetta*, 1900, 30, i, 175—186).—*Methylethyl- $\alpha$ -propionothetine bromide*,  $SMeEtBr \cdot CHMe \cdot CO_2H$ , prepared by the action of  $\alpha$ -bromopropionic acid on methyl ethyl sulphide, crystallises in deliquescent, transparent plates. Treatment with freshly precipitated silver chloride yields the corresponding *chloride*, which forms a *platinichloride*,  $(C_6H_{12}O_2S)_2 \cdot H_2PtCl_6$ , separating from water in yellowish-brown, triclinic plates melting and decomposing at  $132-133^{\circ}$  [ $a : b : c = 0.96547 : 1 : 0.84245 ; \alpha = 82^{\circ}27' ; \beta = 121^{\circ} ; \gamma = 127^{\circ}23'$ ].

*Methylethyl- $\beta$ -propionothetine bromide*,  $SMeEtBr \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , is obtained as a syrup by the interaction of  $\beta$ -bromopropionic acid and methyl ethyl sulphide in molecular proportion. The *platinichloride*, which separates as a drusy mass of scaly crystals or as microscopic octahedra, melts and decomposes at  $164^{\circ}$ .

Unsuccessful attempts were made to resolve these thetines by means of *Penicillium glaucum*, *Mucor mucedo*, and *Beggiatoa* (compare Pope and Peachey, *Proc.*, 1900, 16, 12, 43).

T. H. P.

**Energy of some Hydroxysulphonic Acids.** By F. COJAZZI (*Gazzetta*, 1900, 30, i, 187—188).—The velocities of hydrolysis of methyl acetate by means of hydroxymethane-, hydroxyethane-, and hydroxypentane-sulphonic acids has been measured, and also the electrical conductivities of the sodium salts of these acids. The acids are very strongly dissociated, the value 0.97 being obtained for  $\mu_e/\mu_x$  with dilutions of 256 to 512 litres. Neither Ostwald's, nor van't Hoff's, nor Rudolphi's dissociation formula gives a constant value. The velocities of reaction of the acids are in each case slightly less than the values for the isomeric alkyl hydrogen sulphates.

T. H. P.

**Iodation of Fatty Acids.** By W. ZERNOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1029—1033).—By the interaction of *isobutryl chloride*

(1 mol.), sulphur monochloride ( $\frac{1}{2}$  mol.), and iodine, hydrogen chloride is evolved, sulphur deposited, and  $\alpha$ -iodoisobutyryl chloride obtained; on hydrolysis, the latter yields  $\alpha$ -iodoisobutyric acid,  $C_4H_7O_2I$ , which separates in large, flat needles, or from a mixture of acetone and light petroleum, in long, well-developed transparent prisms. It melts at  $73^\circ$  and dissolves readily in alcohol, ether, or acetone, and to a less extent in light petroleum or water; it turns brown in 2 or 3 days, even when kept in a desiccator in the dark.

Schützenberger's method (*Compt. rend.*, 1868, i, 1344) of preparing iodoacetic acid, namely, acting on the anhydride of the acid with iodine and iodic acid, was applied to isobutyric acid, but no crystallisable product was obtained.

T. H. P.

**$\beta$ -Methylethylhydracrylic Acid and  $\beta$ -Methylethylacrylic Acid.** By ARISTARCH POKROVSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 65—69).— $\beta$ -Methylethylhydracrylic acid,  $OH \cdot CMeEt \cdot CH_2 \cdot CO_2H$ , is obtained by oxidising methylethylallylcarbinol with dilute aqueous potassium permanganate as a transparent, syrupy liquid readily soluble in water, alcohol, or ether. Its calcium salt separates in laminae; the barium salt forms radiating fibrous aggregates, the fibres having approximately straight extinction; the zinc salt, which forms slender, prismatic crystals, and the silver salt are less soluble in water than the preceding salts; the copper and lead salts separate from water in resinous masses, the former slowly crystallising on standing in a desiccator.

$\beta$ -Methylethylacrylic acid,  $CMeEt \cdot CH \cdot CO_2H$ , prepared from the hydracrylic acid by dehydration with sulphuric acid, forms a viscous liquid, readily soluble in water, alcohol, or ether; the silver salt separates from water as a flaky precipitate.

T. H. P.

**$\beta$ -Methyl *tert*-Butylhydracrylic Acid.** By ZINOVY TALANZEFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 69—72).—This acid, which was obtained by Gnedin (*Abstr.*, 1898, i, 291) by oxidising methyl-*tert*-butylallylcarbinol with potassium permanganate, but was not investigated by him, separates, on gently evaporating its ethereal solution, in oblong monoclinic plates melting at  $72$ — $73^\circ$ ; angle of extinction,  $42^\circ$ . It dissolves readily in alcohol or ether, but only slightly in water. The sodium and calcium salts both separate from water in dark, badly formed crystals; the magnesium salt is decomposed in aqueous solution, but separates from dilute alcohol, whilst the normal zinc salt could not be prepared; the silver salt crystallises from water in slender needles.

T. H. P.

**Action of Caro's Reagent on Ketones.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 858—864. Compare this vol., i, 133 and 206).—When a solution of benzoyl peroxide in ether is treated with an atomic proportion of sodium dissolved in alcohol, the sodium derivative of benzoyl hydrogen peroxide,  $COPh \cdot O \cdot ONa$ , is precipitated; the substance liberates iodine from potassium iodide, and converts aniline into nitrosobenzene, confirming the authors' opinion that Caro's reagent contains an acid analogous to 'chamber crystals.'

The fact that acetone peroxide prepared by Caro's reagent melts at  $132$ — $133^\circ$ , whilst the peroxide prepared by Wolfenstein melts at

94—95° (compare this vol., i, 133), is due to the circumstance that the former substance has a molecular weight corresponding with that required for the formula  $(C_3H_6O_2)_2$ , the compound of lower melting point having the formula  $(C_3H_6O_2)_3$ .

When chloroacetone is treated with Caro's reagent, the product consists of an oil and a crystalline substance, which melts at 104—105°, and is indifferent towards potassium iodide; it explodes when struck.

The yield of the lactone of  $\epsilon$ -hydroxy- $\beta\zeta$ -dimethyloctioic acid from menthone is increased by adding glacial acetic acid to the reagent before the addition of the ketone. The *ethyl* ester of  $\epsilon$ -hydroxy- $\beta\zeta$ -dimethyloctioic acid, prepared from the lactone and alcoholic sulphuric acid, boils at 152—155° under 15 mm. pressure.

*Hydroxymethylhexoic acid*,  $C_7H_{14}O_3$ , is a syrup, forming a crystalline *silver* salt; the *ethyl* ester, produced by the action of Caro's reagent on alcoholic methylcyclohexanone, boils at 141—142.5° under 15 mm. pressure.

Suberone *peroxide*,  $C_7H_{12}O_2$ , prepared by adding suberone to a cold mixture of potassium persulphate, alcohol, and the monohydrate of sulphuric acid, crystallises from ether in rhombic leaflets, and melts at 99—100°; it is indifferent towards potassium iodide and boiling caustic soda.

$\zeta$ -*Hydroxyheptoic (heptane-7-ol-1-oic) acid*,  $C_7H_{14}O_3$ , is a syrup, forming crystalline *calcium*, *zinc*, *lead*, and *silver* salts; the *ethyl* ester occurs in the filtrate from suberone peroxide, and boils at 146—155° under 15 mm. pressure.

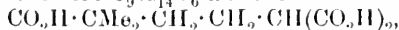
$\zeta$ -*Iodoheptoic acid*,  $C_7H_{13}O_2I$ , obtained on heating the foregoing acid with hydriodic acid, crystallises in lustrous leaflets, and melts at 49—51°.

$\zeta$ -*Bromoheptoic acid*,  $C_7H_{13}O_2Br$ , melts at 30—31°. Potassium permanganate oxidises hydroxyheptoic acid to pimelic acid.

M. O. F.

**Constitution of *iso*-Lauronic Acid.** By G. BLANC (*Compt. rend.*, 1900, 130, 840—841).—When *isolauronic* acid is reduced with sodium amalgam in alkaline solution, it yields dihydroisolauronic acid,  $C_9H_{14}O_3$ , which is a  $\gamma$ -ketonic acid and not a  $\beta$ -hydroxy-acid as Perkin has stated (*Trans.*, 1898, 73, 804). When this is oxidised with very dilute sodium hypobromite solution, it yields a new acid,  $C_9H_{14}O_6$ , which melts at 167—168°, loses carbon dioxide, and is converted into *aa*-dimethyladipic acid.

It follows that the acid  $C_9H_{14}O_6$  has the constitution



whilst dihydroisolauronic acid is  $CMe_2 \cdot \begin{smallmatrix} CO-CH \\ | \quad | \\ CH_2 \cdot CH_2 \end{smallmatrix} \cdot CH \cdot CO_2H$ , and

*isolauronic* acid,  $CMe_2 \cdot \begin{smallmatrix} CO-CH \\ | \quad | \\ CH_2 \cdot CH_2 \end{smallmatrix} \cdot C \cdot CO_2H$  (compare *Abstr.*, 1899, i, 925).

C. H. B.

**$\beta$ -Hydroxy-*aa\beta*-Trimethyladipic Acid.** By EDMOND E. BLAISE (*Compt. rend.*, 1900, 130, 1033—1036).—Methyl levulate condenses with methyl bromoisobutyrate in the presence of zinc to form a compound which, on treatment with dilute sulphuric acid, yields the

*methyl ester*,  $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{CO} \text{---} \text{O} \end{matrix} > \text{CMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Me}$ , of the lactonic acid corresponding with  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethyladipic acid. This is an oily liquid which boils at  $162\text{--}165^\circ$  under 19 mm. pressure, and has a sp. gr. 1.1334 at  $9^\circ/9^\circ$ ; it is completely decomposed by alkalis, with the formation of levulic and isobutyric acids, but when hydrolysed with dilute hydrochloric acid, it furnishes the *lactonic acid*, which crystallises in large prisms melting at  $108\text{--}109^\circ$ . The *ethyl ester*, which could only be obtained by the interaction of the sodium salt with ethyl iodide, boils at  $287\text{--}289^\circ$ . When heated to  $175^\circ$ , the lactonic acid loses carbon dioxide, and is converted into a mixture of a *lactone*,  $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{CO} \text{---} \text{O} \end{matrix} > \text{CMe} \cdot \text{CHMe}_2$ , which boils at  $234\text{--}236^\circ$  and has a faint odour of camphor, and an unsaturated acid [ $\gamma\delta$ -dimethyl- $\Delta\beta$ -hexenoic acid],  $\text{CHMe}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , isomeric with the lactone, which boils at  $235\text{--}237^\circ$ . This acid forms an *ethyl ester* boiling at  $203\text{--}204^\circ$ , and reacts readily with bromine (2 atoms) to form an additive product which crystallises from benzene in small plates melting and decomposing at  $141\text{--}142^\circ$ ; it also yields a crystalline compound with hydrogen bromide, but when boiled with hydrobromic acid is converted into the isomeric lactone. N. L.

**Alkali Copper Tartrates and Fehling's Solution. II.** By FRIEDRICH BULLNHEIMER and E. SEITZ (*Ber.*, 1900, 33, 817—823. Compare Abstr., 1899, i, 868).—Alkali copper tartrates of the type  $\text{C}_4\text{H}_2\text{O}_6\text{CuM}'_2$  are obtained by dissolving copper tartrate in an excess of 4 per cent. aqueous alkali hydroxide at a temperature below  $50^\circ$ , or by digesting a solution of the normal alkali tartrate with the calculated quantity of copper hydroxide for 1 hour on the water-bath.

The *sodium copper d-tartrate*,  $\text{C}_4\text{H}_2\text{O}_6\text{CuNa}_2 \cdot 2\text{H}_2\text{O}$ , forms small, bright blue, lustrous crystals, and dissolves in water with an alkaline reaction; after expelling the water of crystallisation, the salt dissolves in water, giving a *green* solution, which after 2 days becomes blue. The corresponding *sodium copper l-tartrate* has similar properties, and the analogous *racemate* (with  $4\text{H}_2\text{O}$ ) has already been described (Werther, *Annalen*, 1844, 52, 301). Although *potassium* and *lithium copper racemates* (with 3 and  $4\text{H}_2\text{O}$  respectively) were prepared, the analogous *d*- and *l*-tartrates could not be obtained, owing to decomposition occurring. Ammonia gives rise either to the tetrammonium tartrates already described (*loc. cit.*), or to a salt which approximates to the formula  $\text{C}_4\text{H}_2\text{O}_6\text{Cu}(\text{NH}_3)_2\text{Cu} + 4\text{H}_2\text{O}$ .

A third class of salts is obtained by just neutralising a solution of copper tartrate with an alkali carbonate or hydroxide; these salts are bluish-green in solution, cannot be obtained crystalline, and show a great tendency to decompose, although they are not split up by carbon dioxide like the salts of the other two classes (compare also Werther, *Jahresber.*, 1844, 432, and Masson and Steele, *Trans.*, 1899, 75, 725).

Luff has described (*Zeit. ges. Brauw.*, 1898, 21) a potassium copper citrate,  $\text{C}_6\text{H}_8\text{O}_2\text{Cu}(\text{CO}_2\text{K})_6 + 6\text{H}_2\text{O}$ ; if the authors' method of preparation of the alkali copper tartrates be applied to citric acid, the *salt*,



$C_6H_8O_2Cu(CO_2K)_6 \cdot OK \cdot C_3H_4(CO_2K)_3 + 12H_2O$ , is obtained in beautiful, dark blue crystals.

In the alkali copper tartrates described, it appears that the hydrogen of the original hydroxyl groups of tartaric acid has been replaced by copper, thus  $\begin{matrix} CO_2K \cdot CH \cdot O \\ CO_2K \cdot CH \cdot O \end{matrix} > Cu$ ; in the ditartrates, either the union between the molecules  $C_4H_2O_6CuM_2$  and  $C_4H_2O_6M_4$  is molecular, or they are combined through the medium of a copper atom, as in the formula  $[CO_2Na \cdot CH(ONa) \cdot CH(CO_2Na) \cdot O]_2Cu$ .

W. A. D.

**Stereoisomeric Forms of Citral.** By FERDINAND TIEMANN (*Ber.*, 1900, 33, 877—885. Compare Abstr., 1899, i, 250).—[With MAX KERSCHBAUM.]—The view expressed by Tiemann (*loc. cit.*), according to which ordinary citral consists of two geometrical isomerides, is now confirmed by the isolation of 'citral *b*'; this operation depends on the fact that citral *b*, derived from the semicarbazone which melts at  $171^\circ$ , combines with cyanoacetic acid less rapidly than citral *a*.

Citral *b* has the chemical properties of citral *a*, but it boils at  $102\text{--}104^\circ$  under 12 mm. pressure, has a sp. gr. 0.888 at  $19^\circ$ , and the index of refraction 1.49001. The oxime boils at  $136\text{--}138^\circ$  under 11 mm. pressure; the  $\beta$ -naphthacinchonic acid melts at  $200^\circ$ .

*b*-Citralidenecyanoacetic acid crystallises from petroleum in yellowish needles, and melts at  $94\text{--}95^\circ$ .

The  $\psi$ -ionone, prepared from citral *b*, yields a semicarbazone which melts at  $143\text{--}144^\circ$ , and differing from the derivative of  $\psi$ -ionone obtained from citral *a*.

The proportion of citral *b* in lemon grass oil, ordinary citral, and verbenal oil has been determined by the cyanoacetic acid method.

M. O. F.

**Citronellalacetal.** By CARL D. HARRIES (*Ber.*, 1900, 33, 857).—Citronellaldimethylacetal,  $CM_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH(OMe)_2$ , prepared by treating citronellal with a 1 per cent. solution of hydrogen chloride in methyl alcohol (Fischer and Giebe, Abstr., 1898, i, 167), is also produced by the action of methyl iminoformate hydrochloride (Claisen, Abstr., 1898, i, 421). It boils at  $110\text{--}112^\circ$  under 12—13 mm. pressure, and has sp. gr. 0.885 at  $11.5^\circ$ .

M. O. F.

**Function of Aluminium Chloride in the Friedel-Crafts' Reaction.** By GUSTAVE PERRIER (*Ber.*, 1900, 33, 815—816).—The formation of ketones from acid chlorides by means of aluminium chloride takes place in two stages, (1),  $2RCOCl + Al_2Cl_6 = (RCOCl)_2 \cdot Al_2Cl_6$ ; (2),  $(RCOCl)_2 \cdot Al_2Cl_6 + C_mH_n = 2HCl + (RCO \cdot C_mH_{n-1})_2 \cdot Al_2Cl_6$ , the additive compounds assumed to be formed in these equations being readily isolated in a crystalline form. To obtain the ketones, it is best to prepare the additive compound of the acid chloride and aluminium chloride first, then to add the hydrocarbon, and after the elimination of hydrogen chloride, to decompose the additive compound of the ketone by water.

Analogous additive compounds can be isolated when ferric chloride is used instead of aluminium chloride (compare Nencki, Abstr., 1897, i, 520; 1899, i, 879).

W. A. D.

**Electrolytic Oxidation of Ketoximes: New Method of Preparing Aliphatic Nitroso-compounds.** By JULIUS SCHMIDT (*Ber.*, 1900, 33, 871—877).—When ketoximes are electrolysed in dilute sulphuric acid solution, they yield pseudonitroles. For instance, acetoxime is converted into propylpseudonitrole, along with an oily compound,  $C_3H_6O_4N_2$ , which spontaneously undergoes decomposition during the course of a few hours; the oil gives Liebermann's reaction, and is very volatile, the vapour producing extreme irritation in the mucous membrane.

M. O. F.

**Rhodoose, a New Sugar of the Methylpentose Series.** By EMIL VOTOČEK (*Zeit. Zuck.-Ind. Böhm.*, 1900, 24, 248—257).—By hydrolysing convolvulin with dilute sulphuric acid, a mixture of 1 mol. of glucose with 2 mols. of a new methylpentose, to which the name *rhodoose* is given, is obtained. The glucose can be separated by fermentation, the new sugar being non-fermentable. When prepared from its methylphenylhydrazone, it slowly crystallises in microscopic needles; it is soluble in water and has a specific rotation  $[\alpha]_D$  about  $+36^\circ$ . Its *phenylosazone* melts at  $170^\circ$  and is soluble in acetone; the *diphenylhydrazone*,  $C_{18}H_{22}O_4N_2$ , separates from boiling alcohol in nearly white needles melting at  $199^\circ$ , and is reconverted into rhodoose by the action of benzaldehyde. By means of saturated alcoholic hydrogen chloride, rhodoose is with difficulty converted into a *methylethylpentoside* having a specific rotation  $[\alpha]_D$  about  $+30^\circ$ .

T. H. P.

***d*-Sorbose and *l*-Sorbose ( $\psi$ -Tagatose) and their Configuration.** By C. A. LOBRY DE BRUYN and WILLIAM ALBERDA VAN EKENSTEIN (*Réc. Trav. Chim.*, 1900, 19, 1—11).—This paper contains a more detailed account of the purification and physical constants of *l*-sorbose ( $\psi$ -tagatose) and its derivatives (compare this vol., i, 208). *Methyl l-sorboside*, prepared by treating *l*-sorbose with methyl alcohol containing hydrogen chloride, melts at  $119^\circ$  and has  $[\alpha]_D$   $88.5^\circ$ .

When reduced with sodium amalgam in a slightly alkaline solution, *d*-sorbose yields *d*-sorbitol and *d*-iditol, which, when treated with benzaldehyde and 50 per cent. sulphuric acid, are converted respectively into dibenzylidene-*d*-sorbitol and tribenzylidene-*d*-iditol; these substances are separated from one another by crystallisation from acetone, in which the latter is only sparingly soluble. *Tribenzylidene-d-sorbitol* is produced when concentrated hydrochloric acid is employed as the condensing agent.

The two alcohols may also be separated by the aid of their methylene derivatives; these compounds are produced by the action of formaldehyde in the presence of concentrated hydrochloric acid. *Trimethylene-d-sorbitol* melts at  $202^\circ$  and has  $[\alpha]_D$   $-30^\circ$ ; *trimethylene-d-iditol* melts at  $262^\circ$  and has  $[\alpha]_D$   $-8^\circ$ ; the latter is very sparingly soluble in alcohol, whereas the former readily dissolves in this medium.

*Dibenzylidene-l-sorbitol*, obtained from *l*-sorbose, melts at  $160^\circ$  and has  $[\alpha]_D$   $-28^\circ$ ; *tribenzylidene-l-iditol*, which accompanies this substance, is identical with the compound prepared from *l*-idonic acid; *l*-iditol is obtained in a crystalline form by the hydrolysis of its benzylidene derivative.

The *methylene* derivatives of *l*-sorbitol and *l*-iditol are the antipodes

of those of the *d*-series, they melt at  $203^{\circ}$  and  $262^{\circ}$  respectively, and have  $[\alpha]_D$   $30^{\circ}$  and  $8^{\circ}$ .  
G. T. M.

**Cryoscopy of Tanret's Rhamninose and Rhamnintrionic Acid.** By A. PONSOT (*Bull. Soc. Chim.*, 1900, [iii], 23, 145—147. Compare this vol., i, 78).—The author considers that the conclusions drawn by C. and G. Tanret from their cryoscopic determinations of the molecular weights of rhamninose and of rhamnintrionic acid are not fully justified. In this, as in other similar cases, definite results can only be established by extended series of experiments under different conditions.  
N. L.

**Solubility of Salts of Calcium, Iron, and Copper in Sucrose Solutions.** By F. STOLLE (*Zeit. Ver. Deut. Zuck-Ind.*, 1900, 321—341).—The solubilities of calcium sulphate and sulphide, ferric oxide, ferric hydroxide, triferrie tetroxide, ferrous sulphide, and copper sulphide in sucrose solutions of varying concentration were determined at different temperatures. The numbers obtained are given in detail, and lead to the following conclusions: In the case of calcium sulphate, the amount dissolved by a given volume of sugar solution at a fixed temperature decreases as the concentration of the solution increases. Further, at low temperatures ( $40^{\circ}$ ), a sugar solution does not dissolve as much calcium sulphate as would the water contained in the solution; at temperatures of about  $50$ — $70^{\circ}$ , solutions containing up to about 30 per cent. of sugar dissolve more of the salt than their contained water would, whilst with stronger solutions the opposite is the case; at still higher temperatures, the behaviour is similar to that at low temperatures. With calcium sulphide, the solubility increases very quickly with the concentration of the sugar solution and also with the temperature; the solubility curve of any particular solution, like that for water, first falls and then rises as the temperature increases, the temperature of minimum solubility varying with the concentration. Calcium sulphide suffers decomposition when dissolved in sugar solutions. As regards the iron compounds examined, ferric oxide is the only one which gives rise to a sucrate, while with none of them was any inverting action observable; the solubilities of ferric oxide and hydroxide are extremely small, those of triferrie tetroxide and ferrous sulphide somewhat greater, whilst they all give a yellow colour to the solutions. Copper sulphide is very much more soluble in sugar solutions than is ferrous sulphide, and its solubility increases considerably as the temperature rises.  
T. H. P.

**Action of Silver Oxide and of Hydroxylamine on Bromoamines.** By NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1033—1062. See this vol., i, 277).—The action of silver oxide on  $\beta$ -bromoaminohexane yields methyl butyl ketone and  $\beta$ -hexylhydrazine, and on oxidising the latter with alkaline potassium ferricyanide solution, normal hexane is obtained. Similarly, normal heptane and octane are produced by the oxidation of  $\delta$ -heptylhydrazine and  $\beta$ -octylhydrazine respectively; and 1-bromo-amino-3-methylcyclohexane yields with silver oxide the corresponding hydrazine which, with potassium

ferricyanide and alkali, gives methylcyclohexane. When *l*-menthylhydrazine [ $\text{Pr}:\text{N}_2\text{H}_3 = 1:2$ ] is oxidised in this way, in absence of alkali, it yields a mixture of menthane with a small proportion of menthene; menthane alone is obtained if alkali is present, whilst if the oxidation is carried out in hydrochloric acid solution, menthene and a menthyl chloride are obtained.

The above-described method of preparation of hydrocarbons, namely, the oxidation of hydrazines by means of alkaline potassium ferricyanide solution, offers the advantages that, firstly, all the operations involved are quickly completed, and, secondly, no isomeric change is possible, the structure of the hydrocarbon obtained being hence known when the constitution of the amine employed is known.

The action of the halogen hydracid salts of hydroxylamine on the dibromoamines is partly to convert the latter into the corresponding amines, and partly to form first an intermediate diazo-compound, which is, in its turn, resolved by the halogen hydracid into an unsaturated hydrocarbon on the one hand, and a halogenated hydrocarbon on the other. Thus hydroxylamine hydrochloride with ethyldibromoamine gives ethylene and ethylene dibromide, whilst with *iso*amyl dibromoamine, *iso*amyl bromide is formed. Hydroxylamine hydrobromide and heptyldibromoamine,  $(\text{CHPr}_2\cdot\text{NBr}_2)$ , interact with formation of a heptyl bromide boiling at  $155\text{--}170^\circ$ . With  $\alpha$ -methylheptyldibromoamine, hydroxylamine hydrochloride yields  $\alpha$ -methylheptylamine, together with a mixture of the corresponding octylene and a bromo-compound. In the case of benzyl dibromoamine, no bromotoluene is obtained, as when acted on by hydroxylamine hydrochloride, a mixture of benzyl chloride and bromide is formed, whilst with the hydrobromide it yields benzyl bromide alone.

In alkaline alcoholic solution, the action of hydroxylamine on dibromoamines takes a course differing from that followed in acid solution: the first stage of the reaction gives rise to a hydrazone and a diazo-compound, the latter then decomposing with formation of an alcohol, an unsaturated hydrocarbon, and an ethyl derivative. Thus, in the case of menthyldibromoamine, menthane, menthyldiazo-compound and diazomenthane are first formed, subsequent decomposition of the diazo-compound yielding menthene, menthol, and the ethyl derivative of menthol,  $\text{C}_{10}\text{H}_{19}\cdot\text{OEt}$ .

T. H. P.

**Acetylation of Primary and Secondary Amines.** By L. MUSSELIUS (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 29–35).—The acetates of a number of amines were heated in sealed tubes in a bath of nitrobenzene vapour ( $212^\circ$ ). The relative velocity of the reaction, which proves to be reversible for both primary and secondary amines, was measured by determining the amount of change produced after half an hour's heating, and the limit of the reaction on prolonged heating was also observed. In the case of methylamine acetate, equilibrium is attained when 80.08 per cent. of the salt is converted into the corresponding substituted amide; this proportion rises as the molecular weight of the primary amine increases, its value for heptylamine being 97.75 per cent. The velocity of reaction also rises with

the molecular weight, being 78.0 per cent. for methylamine and 95.63 per cent. for heptylamine. Both the velocity and limit of reaction for ammonium acetate are intermediate between the corresponding values for the methylamine and ethylamine salts. For secondary amines, the results are given in the following table :

	Velocity of reaction.	Limit of change.
Dimethylamine .....	84.80 per cent.	92.23 per cent.
Diethylamine .....	40.74 "	78.32 "
Dipropylamine .....	51.65 "	84.22 "
Diisobutylamine .....	41.59 "	82.11 "
Diisoamylamine .....	50.80 "	84.09 "

It will be seen that the numbers alternately rise and fall as the molecular weight of the amine increases. T. H. P.

**Reaction for distinguishing Differently Substituted Amines.** By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 40—41).—The observation of Musselius (preceding abstract) that, when warmed with acetic acid, tertiary amines are not acetylated, whilst primary and secondary are, although at very different speeds, serves as the basis of a method for distinguishing these amines. The amine is sealed up in a glass tube with an equivalent proportion of acetic acid and heated in a bath of nitrobenzene vapour for 30 minutes, after which it is quickly cooled, broken, and the contents mixed with a few c.c. of 96 per cent. alcohol, and titrated with alcoholic potash in presence of phenolphthalein. Primary amines are in general acetylated to the extent of about 87.5 to 95.5 per cent., the proportion for secondary amines being about 40 to 50 per cent. T. H. P.

**Influence of the Side-chain on the Properties of Open- and Closed-chain Carbon Compounds. V. Velocity of Combination of Secondary Amines with Alkyl Bromides.** By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 41—45).—In the following table, the mean velocities of combination of allyl bromide with various amines are given.

Ammonia .....	1380		
Methylamine ..	8302	Dimethylamine ...	30833
Ethylamine .....	3807	Diethylamine .....	4952
Propylamine ...	3783	Dipropylamine ...	2910
isobutylamine ...	1240	Diisobutylamine ...	718
isoAmylamine ...	2985	Diisoamylamine ...	1384

The same kind of variation is shown here as was found by Musselius (this vol., i., 334) for the velocities of reaction of the secondary amines with acetic acid. In the case of methylamine and ethylamine, the speed of combination with alkyl bromides is increased by further replacement of the hydrogen of the amino-group, whilst with propyl-, isobutyl- and isoamyl-amines the opposite takes place. This is seen from the following numbers :

$\text{NH}_3 + \text{MeBr} \dots$	5471		
$\text{MeNH}_2 + \text{MeBr} \dots$	31910	$\text{EtNH}_2 + \text{C}_3\text{H}_5\text{Br}$	3807
$\text{Me}_2\text{NH} + \text{MeBr} \dots$	59954	$\text{Et}_2\text{NH} + \text{C}_3\text{H}_5\text{Br}$	4952
$\text{Me}_3\text{N} + \text{MeBr} \dots$	47437	$\text{Et}_3\text{N} + \text{C}_3\text{H}_5\text{Br}$	757
$\text{Pr}^a\text{NH}_2 + \text{C}_3\text{H}_5\text{Br}$	3783	$\text{Pr}^a_2\text{NH} + \text{C}_3\text{H}_5\text{Br}$	2910
$\text{C}_4\text{H}_9\beta\text{NH}_2 + \text{C}_3\text{H}_5\text{Br}$	1240	$(\text{C}_4\text{H}_9\beta)_2\text{NH} + \text{C}_3\text{H}_5\text{Br}$	718
$\text{C}_5\text{H}_{11}\beta\text{NH}_2 + \text{C}_3\text{H}_5\text{Br}$	2985	$(\text{C}_5\text{H}_{11}\beta)_2\text{NH} + \text{C}_3\text{H}_5\text{Br}$	1384

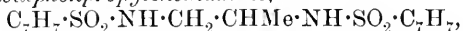
T. H. P.

**Ethylenetrimethylenediamine and Methylpiperazine.** By WERNER ESCH and WILHELM MARCKWALD (*Ber.*, 1900, **33**, 761—764. Compare Abstr., 1899, i, 750).—*Ethylenetrimethylenediaminecarbamide*,  $\text{NH} \left\langle \begin{smallmatrix} (\text{CH}_2)_2 \\ (\text{CH}_2)_3 \end{smallmatrix} \right\rangle \text{N} \cdot \text{CO} \cdot \text{NH}_2$ , which separates in tablets on evaporating ethylenetrimethylenediamine hydrochloride with potassium cyanate, crystallises from hot water, and melts at  $251^\circ$ . The *diphenyldithiocarbamide*,  $\text{C}_5\text{H}_{10}\text{N}_2(\text{CS} \cdot \text{NHPh})_2$ , separates from an alcoholic mixture of the base with 2 mols. phenylthiocarbimide, in glistening, colourless prisms, melts at  $216\text{--}217^\circ$ , and is only slightly soluble

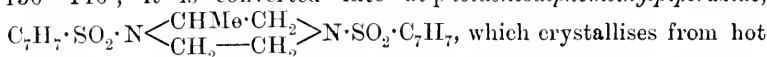
in most solvents. The *thiocarbamate*,  $\text{N} \left\langle \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CS} \text{---} \text{S} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{NH}_2$ ,

separates in white crystals on adding carbon disulphide to an alcoholic solution of the base, and melts and decomposes at  $233^\circ$ . *Diphenylazo-ethylenetrimethylenediamine*,  $\text{C}_5\text{H}_{10}\text{N}_2(\text{N}_2\text{Ph})_2$ , separates from alcohol or light petroleum in yellow crystals and melts at  $118^\circ$ .

*Di-p-toluenesulphonylpropylenediamine*,



separates from hot alcohol or benzene in white crystals, and melts at  $103\text{--}104^\circ$ . By heating the sodium salt with ethylene bromide at  $130\text{--}140^\circ$ , it is converted into *di-p-toluenesulphomethylpiperazide*,



which crystallises from hot alcohol and melts at  $174^\circ$ . When hydrolysed with hydrogen chloride, it yields methylpiperazine (Stoehr, Abstr., 1895, i, 569), which can thus be prepared without difficulty. The *aurichloride*,  $\text{C}_5\text{N}_2\text{H}_{12} \cdot 2\text{HAuCl}_4$ , forms yellow crystals and melts and decomposes at  $220^\circ$ . The *thiocarbamate*,  $\text{C}_6\text{H}_{12}\text{N}_2\text{S}_2$ , separates in white crystals on adding carbon disulphide to an alcoholic solution of the base, and melts and decomposes at  $193\text{--}194^\circ$ .

T. M. L.

**Dimethylenimine.** By WILHELM MARCKWALD (*Ber.*, 1900, **33**, 764—766. Compare Abstr., 1899, i, 749; this vol., ii, 149, and Duden and Macintyre, this vol., i, 302).—The author reaffirms his statement that the compound prepared by removing hydrogen bromide from bromoethylamine is not a primary base (vinylamine), but a secondary base (dimethylenimine), and that ‘vinylamine’ is not yet known. He regards Hinsberg’s reaction as more trustworthy than the alkylation method advocated by Duden (this vol., i, 282) for distinguishing primary and secondary bases, since methyl iodide often

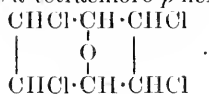
causes opening of the ring in cyclic bases such as those of the pyrrolidine and piperidine series. T. M. L.

**Hexethylidenetetramine.** By RICHARD KUDERNATSCHEW (*Monatsh.*, 1900, 21, 137—147).—*Hexethylidenetetramine*,  $C_{12}H_{24}N_4$ , prepared by heating aldehyde-ammonia with 20 per cent. aqueous ammonia in sealed tubes at 140—150°, crystallises from hot water in monoclinic prisms, which contain  $6H_2O$  and melt at 96°; when anhydrous, it melts at 102°; it is easily soluble in organic solvents with the exception of chloroform and benzene. It forms an indefinite *additive product* with benzoyl chloride,  $C_{12}H_{24}N_4 \cdot 3PhCOCl$ , and the unstable *hexabromide*,  $C_{12}H_{24}N_4Br_6$ , and *tetrabromide*,  $C_{12}H_{24}N_4Br_4$ . The *hydrochloride*,  $C_{12}H_{24}N_4 \cdot 3HCl$ , forms colourless, monoclinic prisms, which begin to decompose at 250°, the *platinichloride* decomposes at 200°, and the *hydrobromide* melts and decomposes at 244°. By the action of nitrous acid on hexethylidenetetramine, an undetermined compound,  $C_{19}H_{35}O_5N_{11}$ , is obtained; it melts and decomposes at 212°, gives the Liebermann reaction, and is decomposed by acids. R. H. P.

**Structure of Acid Amides.** By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 35—40).—The author is of opinion that the methods of formation and the reactions of the acid amides accord better with the formula  $R \cdot CO \cdot NH_2$  than with the enolic formula  $R \cdot C(OH) : NH$ . According to the latter formula, in the formation of acetamide from acetic acid and ammonia, and of mono-substituted acetamides by the action of acetic acid on primary amines (see Musselius, this vol., i, 334), the water eliminated is composed of the oxygen atom of the carbonyl group of the acetic acid, and two hydrogen atoms from the ammonia or the amino-group; further, the formation of di-substituted acetamides from acetic acid and secondary amines would require one of the alkyl groups to leave the nitrogen atom and replace the hydrogen of the hydroxyl group. Also the enolic formula for acetyldimethylamide does not give a good explanation of the re-formation of dimethylamine by the taking up of water. The conversion of acetamide derivatives into those of the imino-acids with intermediate formation of nitriles is regarded as due to the fact that the latter are capable of reacting with hydroxy-compounds in the following manner:  $R \cdot C : N + H \cdot OR' = R \cdot C(OR') : NH$ . T. H. P.

**Action of Chlorine Monoxide on Benzene.** By ROLAND SCHOLL and WILHELM NÖRR (*Ber.*, 1900, 33, 723—728).—Chlorine monoxide is readily absorbed by benzene at 0° in the dark. The products of the reaction consist of  $\alpha$ - and  $\beta$ -benzene hexachlorides, 2 : 4 : 6-trichlorophenol and a new compound,  $C_6H_6OCl_3$ . This is an amorphous, white mass, which softens at 60°, melts at 70—75°, and decomposes at about 200°; it is soluble in alcohol, and is decomposed by alcoholic soda and by potassium permanganate, whilst it is not attacked by fuming nitric acid, bromine, acetic anhydride, or phenylhydrazine. On distillation, under diminished pressure, it yields two oils, boiling under the ordinary pressure at 200° and 305—310° respectively, but the nature and

composition of these has not yet been ascertained. It seems probable that the new compound is a tetrachloro-*p*-hexamethylene oxide,



A. H.

**Isomorphous Replacement of Halogens and Hydroxyl.** By G. FELS (*Zeit. Kryst. Min.*, 1900, 32, 359—417).—Several examples of the isomorphous replacement of fluorine (rarely chlorine) and hydroxyl are known amongst minerals; amongst benzene derivatives, however, the author shows that there is no isomorphous replacement between the halogens (chlorine, bromine and iodine) and hydroxyl. The paper contains detailed crystallographic descriptions of numerous halogen, nitro- and amino-substitution products of benzene and phenol.

L. J. S.

*as* Iodoso-, *as*-Iodoxy-, and *as*-Iodonium-compounds derived from *m*-Xylene. By CONRAD WILLGERODT and VINCENT ALLEN HOWELLS (*Ber.*, 1900, 33, 841—851).—*m*-Xylene-4-iodochloride, prepared by chlorinating 4-iodo-*m*-xylene in well cooled chloroform and pouring the product into a large quantity of light petroleum, forms stout, yellow needles and melts and decomposes at 91°; it is easily converted by alkalis into the corresponding *iodoso*-compound, the *acetate*,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{I}(\text{OAc})_2$ , of which crystallises from chloroform in large, white prisms, and melts at 128°. The *basic sulphate*,  $[\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{I}(\text{OH})]_2\text{SO}_4$ , the first stable sulphate of an *iodoso*-compound which has yet been prepared, forms well defined crystals and melts and decomposes at 113—115°; the *basic nitrate*,  $\text{C}_8\text{H}_{10}\text{O}_4\text{NI}$ , is a dull yellow, amorphous powder which decomposes at 118°. 4-Iodoxy-*m*-xylene separates from glacial acetic acid as a microcrystalline powder and explodes at 195°.

*Di-as-m-xylyliodonium hydroxide*,  $\text{I}(\text{C}_6\text{H}_3\text{Me}_2)_2 \cdot \text{OH}$ , exists only in solution; the *chloride* forms small, white rhombs and melts at 169°; the *bromide*, thick, white needles melting at 170°, whilst the *iodide* forms beautiful, white leaflets and melts at 148°; the *nitrate* is a white, amorphous powder which melts and decomposes at 161°, and the *dichromate*,  $(\text{C}_6\text{H}_3\text{Me}_2\text{I})_2\text{Cr}_2\text{O}_7$ , an orange mass melting at 145°.

*Iododi-as-m-xylyliodonium hydroxide*,  $\text{C}_6\text{H}_2\text{Me}_2\text{I} \cdot \text{I}(\text{OH}) \cdot \text{C}_6\text{H}_3\text{Me}_2$ , prepared by dissolving the *iodoso*-compound in cold concentrated sulphuric acid and subsequently diluting with ice (compare Meyer and Hartmann, *Abstr.*, 1894, i, 242), is strongly alkaline in solution; the *chloride* is a white, amorphous, sparingly soluble substance, which melts at 127—128°, whilst the *bromide* melts at 119°; the *iodide* crystallises in white leaflets and is easily soluble in chloroform, but insoluble in all other solvents; the *dichromate* explodes at 109°.

*p-Tolyl-as-m-xylyliodonium hydroxide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{I}(\text{OH}) \cdot \text{C}_6\text{H}_3\text{Me}_2$ , yields a *chloride* which crystallises in white needles, and a white, amorphous *mercurichloride*,  $(\text{C}_{15}\text{H}_{16}\text{Cl})_2 \cdot \text{HgCl}_2$ ; the *bromide* and *iodide* form white needles and melt at 179° and 165° respectively, whilst the *dichromate* is an orange powder.

*as-m-Xylyldichloroethyliodonium chloride*,  $\text{C}_2\text{H}_3\text{Cl}_2 \cdot \text{ICl} \cdot \text{C}_6\text{H}_3\text{Me}_2$ , forms stunted, white needles and melts at 171°; the corresponding



*bromide* and *iodide* form slender needles and melt respectively at  $160^{\circ}$  and  $95^{\circ}$ ; the *platinichloride* decomposes at  $139^{\circ}$ . W. A. D.

**Preparation of Iodoso- and Iodoxy-compounds.** By CONRAD WILLGERODT (*Ber.*, 1900, **33**, 853—854).—A controversial paper in which the author reserves for himself certain lines of work.

W. A. D.

**Naphthalene Vapour in Coal Gas.** By RICHARD W. ALLEN (*J. Soc. Chem. Ind.*, 1900, **19**, 209—211).—The author describes experiments which, in his opinion, prove that coal gas containing no appreciable amount of naphthalene vapour still deposits naphthalene in the distributing pipes. It would seem that this must be gradually formed by the action of the hydrocarbon gases on each other in the pipes, but the matter needs further investigation. L. DE K.

**Refraction of Hydrocarbons with Condensed Benzene Nuclei.** By ALBERTO CHILESOTTI (*Gazzetta*, 1900, **30**, i, 149—169).—Measurements have been made of the refractions of dibenzyl, stilbene, tolane, phenanthrene, retene, and fluorene in benzene solution, and of anthracene in naphthalene solution, the influence of the solvent being allowed for by means of Landolt's formula for mixtures. In the following table, the mean experimental numbers for the molecular refractions are given for the line  $H_{\alpha}$ , together with the values calculated from the structural formula, the atomic refractions used being as follows. For the Gladstone formula: carbon 5, hydrogen 1.30, and a double linking 2.40; for the Lorenz and Lorentz formula: carbon 2.48, hydrogen 1.04, and a double bond 1.78.

	$M \cdot \frac{\mu_{H_{\alpha}} - 1}{d}$			$M \cdot \frac{\mu_{H_{\alpha}}^2 - 1}{(\mu_{H_{\alpha}}^2 + 2)d}$		
	Found.	Calc.	Diff.	Found.	Calc.	Diff.
Dibenzyl.....	103.83	102.60	1.23	59.59	59.96	0.37
Stilbene.....	115.43	102.40	13.03	65.44	59.66	5.78
Tolane.....	111.70	99.64	12.06	62.07	58.02	4.05
Anthracene.....	109.34	97.40	11.94	61.15	55.80	5.35
Phenanthrene.....	110.70	99.80	10.9	61.59	57.58	4.01
Retene.....	145.12	130.2	14.92	80.64	75.82	4.82
Fluorene.....	98.30	92.40	5.90	55.28	53.32	1.96

From these numbers, it is seen that of those given dibenzyl is the only compound which obeys the laws of Landolt and Brühl. The values in the above table differ somewhat from those obtained by Gladstone (this *Journal*, 1870, **23**, 147), the greatest deviation being in the case of anthracene, for which Gladstone found the molecular refraction 100.3.

Taking the centric formula for the benzene nucleus, the refractive value of each centric linking is for naphthalene, anthracene, phenanthrene, and pyrené, 1.39, 1.46, 1.54, and 1.48 respectively, the Gladstone molecular refraction formula being used; with the Lorenz and Lorentz

formula, the value is even more constant, the numbers for each centric linking being for benzene 0.89, naphthalene 0.90, anthracene 0.89, and phenanthrene 0.90. Hence centric structural formulæ for aromatic hydrocarbons accord best with their optical properties.

T. H. P.

**Action of Phenylcarbimide and Phenylthiocarbimide on Dibasic Acids.** By ÉLOPHE BÉNECH (*Compt. rend.*, 1900, 130, 920—923).—Diphenylmalonamide results from the action of phenylcarbimide on malonic acid, and the corresponding dianilide is obtained in a similar manner from sebacic acid.

The *dianilide* of azelaic acid, produced by heating the acid with phenylcarbimide at  $140^{\circ}$ , crystallises from methyl alcohol in prismatic needles melting at  $185^{\circ}$ ; it is sparingly soluble in water, benzene, or ether, but dissolves in concentrated nitric acid.

The formation of these anilides is attended by the evolution of carbon dioxide.

Experiments were made with phenylthiocarbimide in order to ascertain whether its action on the dibasic acids is analogous to that of the corresponding carbimide. The reaction follows a similar course in the case of succinic and sebacic acids, the former yielding phenylsuccinimide and the latter its dianilide; carbon oxysulphide is evolved in both cases. Malonic acid, however, when treated with the thiocarbimide, yields diphenylcarbimide and acetanilide, whilst ethylmalonic acid gives rise to butyrylanilide.

G. T. M.

**Oxygen Ethers of Carbamides: Methylisocarbamide.** By JULIUS STIEGLITZ and RALPH H. MCKEE (*Ber.*, 1900, 33, 807—812. Compare Abstr., 1899, i, 594).—Phenylmethylcyanamide (cyanomethylaniline), obtained from the corresponding thiocarbamide, melts at  $30.5^{\circ}$ , and not at  $28^{\circ}$  as stated by Wallach (Abstr., 1899, i, 659). Phenylalkylecyanamides do not combine so readily with ethyl alcohol under the influence of hydrogen chloride as does phenylecyanamide itself; the methyl derivative, for example, requires 14 days, whereas the reaction is complete in the case of phenylecyanamide at the end of 2 days. The addition takes place much more readily in the presence of a small quantity of sodium ethoxide, and is complete at the end of 1 to 2 days. The following generalisation is enunciated: Cyanamides which readily form salts with bases combine most readily with ethyl alcohol under the influence of hydrogen chloride, but cyanamides which are of a more basic character are most readily converted into isocarbamide ethers by the aid of sodium ethoxide.

as-iso *Phenylmethylethylecarbamide* (ethyl iminophenylmethylcarbamide),  $\text{NH}\cdot\text{C}(\text{OEt})\cdot\text{NMePh}$ , is a colourless oil distilling at  $137^{\circ}$  under 21 mm. pressure; its *platinichloride*,  $(\text{C}_{10}\text{H}_{14}\text{ON}_2)_2\cdot\text{H}_2\text{PtCl}_6$ , is brownish-yellow, and melts and decomposes at  $160^{\circ}$ . When heated at  $54^{\circ}$  with dry hydrogen chloride, it yields ethyl chloride and as-methylphenylcarbamide. The isomeric as-isophenylmethylethylecarbamide,  $\text{NH}\cdot\text{C}(\text{OMe})\cdot\text{NEtPh}$ , obtained from phenylethylcyanamide, methyl alcohol, and sodium methoxide distils at  $126^{\circ}$  under 15 mm. pressure.

*Methylisocarbamide* (methyl iminocarbamide),  $\text{NH}_2\cdot\text{C}(\text{OMe})\cdot\text{NH}$ , is obtained as its *hydrochloride* by the action of dry hydrogen chloride at

0° on silver cyanamide suspended in anhydrous methyl alcohol; it may also be obtained by leaving a solution of cyanamide (1 mol.) and hydrogen chloride ( $2\frac{1}{2}$  mols.) in anhydrous methyl alcohol (25 mols.) for 7—14 days, and evaporating to dryness under reduced pressure. After purification by solution in absolute alcohol at 55° and subsequent cooling to -10°, it forms small prisms, melts at 130°, evolving methyl chloride, and is readily soluble in alcohol or water; the *platinichloride*,  $(C_2H_5ON_2)_2 \cdot H_2PtCl_6$ , forms long, orange-yellow needles, melting and decomposing at 178°. J. J. S.

**Influence of the Side Chain on the Properties of Open- and Closed-chain Carbon Compounds. VI. Influence of Chemically Indifferent Solvents on the Comparative Velocity of Reaction in Isomeric Benzene Derivatives.** By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 46—60. Compare Abstr., 1898, i, 186).—In benzene solution, the velocity of reaction of aromatic amines having the amino-group in the side chain with allyl bromide is greater than with methyl bromide, whilst if the amino-group is in the benzene nucleus, the opposite is the case. Using acetone as a solvent, however, no such regularity is observed, as for some compounds with an amino-substituent in the benzene nucleus the velocity constant for combination with allyl bromide is greater than with methyl bromide, for others less, whilst with others again the two are about the same. On the other hand, the velocity constant for the reaction *o*-toluidine + allyl bromide is greater than that for *o*-toluidine + methyl bromide, whether the reaction be carried out in benzene, xylene, bromonaphthalene, acetophenone, *n*-propyl alcohol or methyl alcohol.

The action of allyl bromide on the three toluidines has been studied in various solvents, the results being as follows: In benzene or bromonaphthalene solution, the velocity constant is a maximum for the meta-compound and a minimum for the ortho-base, whilst in acetone, acetophenone, or propyl alcohol, the constant has its greatest value for the para- and its least for the ortho-compound. Similar experiments were carried out for the six xylidines in benzene and acetone.

The acetylation of the three toluidines and the six xylidines was also studied. The speeds of acetylation of the toluidines are decreased in presence of excess of the base, and increased if the acid is in excess.

The conclusion is drawn that chemical reactions taking place in liquid systems of organic compounds proceed in the same way whether an indifferent solvent is present or not. Further, in the case of benzene derivatives, a change in the solvent employed is capable of changing the order of the values of the velocity constants of the reactions of position isomerides. T. H. P.

**Action of Formaldehyde on  $\beta$ -Aromatic Hydroxylamines.** By EUGEN BAMBERGER (*Ber.*, 1900, 33, 941—955. Compare Abstr., 1894, i, 412).—*Diphenylmethylenedihydroxylamine*,  $CH_2(NPh \cdot OH)_2$ , formed when concentrated formaldehyde solution (1 mol.) is added to an alcoholic solution of  $\beta$  phenylhydroxylamine, crystallises in colourless, glistening needles decomposing and melting at 106.5°, and is readily soluble in most organic solvents with the exception of light

petroleum. Its solutions gradually turn yellow owing to its conversion into N-phenylglyoxime ether. With ferric chloride, its solutions give a brownish violet-red colour and with alcoholic copper acetate a dark green; most oxidising agents convert it into nitrosobenzene. Other  $\beta$ -aromatic hydroxylamines behave in a similar manner; the products thus formed show feebly acidic and feebly basic properties and are characterised by the readiness with which they undergo decomposition; mineral acids, alkalis, and even boiling water decompose them, yielding hydrogen and N-aromatic glyoximes which have an intense yellow colour and are identical with the products obtained by von Pechmann (Abstr., 1898, i, 75) by the action of diazomethane on aromatic nitroso-compounds. It is held to be probable that both diphenylmethylenedihydroxylamine and Pechmann's additive product from diazomethane and nitrosobenzene undergo dissociation into the same products, namely, formaldehyde and phenylimide, which then react to give the same final product, N-phenylglyoxime ether.

[With L'ORSA.]—*Di-p-tolylmethylenedihydroxylamine* forms colourless needles melting at  $103^{\circ}$  and may be recrystallised from a mixture of chloroform and light petroleum. Glyoxime N-*p*-tolyl ether melts at  $208^{\circ}$ , and when moistened with acetic acid and boiled with dilute sulphuric acid yields toluquinol; with dilute hydrochloric acid, it yields *p*-toluidine and *o*-chloro-*p*-toluidine.

[With FRED. TSCHIRNER.]—*Di-m-tolylmethylenedihydroxylamine* forms glistening needles melting at  $118^{\circ}$ . *Di-p-chlorophenylmethylenedihydroxylamine* melts at  $103^{\circ}$ , and after resolidifying melts and decomposes at  $140^{\circ}$ ; when freshly precipitated, it dissolves readily in mineral acids and is reprecipitated on the rapid addition of acid carbonates; ferric chloride precipitates *p*-chloronitrosobenzene from the sulphuric acid solution, sodium hydroxide yields di-*p*-chloroazoxybenzene. Glyoxime N-*p*-chlorophenyl ether is best obtained by gently warming the finely divided methylene ether with formaldehyde solution, and crystallises from benzene in glistening, golden-yellow plates melting at  $239$ – $240^{\circ}$ .

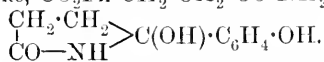
[With ARMAND STIEGELMANN.]—*Di-p-bromophenylmethylenedihydroxylamine* forms glistening needles melting at  $95^{\circ}$ . Glyoxime N-*p*-bromophenyl ether melts at  $230^{\circ}$ , whereas von Pechmann (Abstr., 1898, i, 188) gives the melting point as  $278^{\circ}$ .

[With MARIE BAUM.]—*Di-p-xylyl-O-methylenedihydroxylamine*,  $\text{CH}_2(\text{O}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Me}_2)$ , prepared from 1:4:2-xylylhydroxylamine and formaldehyde, crystallises from a mixture of chloroform and light petroleum in glistening, white needles, melts at  $125^{\circ}$ , and is readily soluble in benzene or chloroform and in hot alcohol or acetone. It is much more stable than the N-ethers described above, and its solutions do not turn yellow; when heated with sulphuric acid, it yields 5-amino-1:4:2-xylenol and with hydrochloric acid, 5-chloro-1:4:2-xyldine, both of which may be regarded as derived from the first products of hydrolysis of xylylhydroxylamine. J. J. S.

Action of Diazomethane on  $\beta$ -Aromatic Hydroxylamines. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1900, 33, 955–959).—In the expectation of obtaining  $\beta$ -phenylhydroxylamine methyl

ether, the authors have studied the action of diazomethane on  $\beta$ -phenylhydroxylamine; the product formed is, however, the same methylene ether as is obtained by the action of formaldehyde on phenylhydroxylamine (compare preceding abstract), nitrogen and hydrogen being evolved. *m*- and *p*-Tolylhydroxylamines behave in a similar manner, whereas 1:4:2-xylylhydroxylamine yields the corresponding O-ether melting at 125° (compare preceding abstract) together with azoxyxylene melting at 111—111.5°. The authors think that the action of the diazomethane is to be attributed to a dissociation into methylene and nitrogen, a conclusion which is supported by the fact that a polymethylene,  $(CH_2)_x$ , is usually obtained as a by-product. It melts at 128° and is insoluble in the usual solvents. J. J. S.

**Crystalline Compounds of Succinimide and the Phenols.** By M. VAN BREUKELEVEEN (*Rec. Trav. Chim.*, 1900, 19, 32—35).—The compound,  $C_6H_6O_2 \cdot C_4H_5O_3N$ , produced by heating together equal mols. of succinimide and phenol dissolved in water or benzene, melts at 58—64°, is readily soluble in water or acetone, and insoluble in carbon disulphide or light petroleum; dry ether resolves it into its generators. The constitution of the substance may be expressed by one or other of the following formulae,  $CO_2Ph \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$  or



The corresponding compound from *p*-bromophenol melts at 74—78°; the *p*-cresol derivative melts at 60—70°; the guaiacol compound could not be obtained crystalline.

The germicidal action of the phenol compound is equal to that of the free phenol. G. T. M.

**Xylylene Hydrosulphides.** By ARTHUR KÖTZ (*Ber.*, 1900, 33, 729—730).—[With SEVIN.]—*o*-Xylylenehydrosulphide, which is prepared by the action of alcoholic potassium hydrosulphide on the corresponding bromide, forms white, odourless crystals, melting at 45—46°, and boils at 160° under 20 mm. pressure. *m*-Xylylene hydrosulphide is a thin oil, which boils at 157° under 15 mm. pressure, and has a faint mercaptan-like odour. The *p*-compound is white and crystalline, has a faint aromatic odour, melts at 46—47°, and boils at 156° under 12 mm. pressure. These three compounds are converted by methylene iodide into odourless mercaptals,  $C_6H_4 \begin{array}{c} CH_2 \cdot S \\ | \qquad | \\ CH_2 \cdot S \end{array} CH_2$ . *o*-Xylylenemercaptal is a colourless, crystalline substance melting at 152—153°; the *m*-compound is amorphous and melts at 74—75°, and the *p*-compound is also amorphous and melts at 152°. A. H.

**Aromatic Esters of Sulphurous Acid.** By M. GEORGESCU (*Chem. Centr.*, 1900, i, 543—544; from *Bul. Soc. Sci. Bucuresti*, 8, 668—681).—Aromatic esters of sulphurous acid are readily prepared by the action of benzenesulphonic chloride on alkaline solutions of phenols at the ordinary temperature. The ester,  $SO_3Ph \cdot C_6H_4Me$ , prepared from *o*-cresol, melts at 39—40°, the *o*-xylyl ester at 72—80°, the *p*-xylyl ester at 51—52°, the guaiacyl ester at 51—52°, the vanillin ester at 68—69°, the methyl salicylate ester,  $PhSO_3 \cdot C_6H_4 \cdot CO_2Me$ , at

41—42°, the *phenolphthalein ester*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{SO}_3\text{Ph})_2$ , at 112—113°, the *salol ester*,  $\text{PhSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Ph}$ , at 80—82°, and the *salicylaldehyde ester*,  $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{COH}$ , at 55°. The preceding compounds crystallise from alcohol. The *carvacryl ester* is an oily liquid and decomposes before it distils. The *creosol ester*,  $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}$ , is a dark yellow oil, and the *eugenol ester* a pale yellow oil. All these compounds are insoluble in water or alkalis, but soluble in organic solvents; they are not attacked by boiling potassium carbonate solution, but are decomposed by boiling with alcoholic potash.

Benzenesulphonic chloride acts on a weak alkaline solution of mononitrophenol as readily as on phenol itself, but the dinitrophenols react less easily, and the trinitrophenols are not attacked. The *o-nitrophenyl ester* crystallises from alcohol and melts at 75°; the *m-nitrophenyl ester* melts at 72—73°, the *p-nitrophenyl ester* at 79—85°, and the *dinitrophenyl ester* at 118°. Only poor yields of these compounds are obtained. The *dinitroresorcinyl ester*,  $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{SO}_3\text{Ph})_2$ , melts at 146°, and the *nitronaphthyl ester* forms large, yellow crystals and melts at 117°.

The compound,  $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , obtained by the action of benzenesulphonic chloride on salicylic acid, melts at 128—130°, and the compound,  $\text{C}_6\text{H}_2(\text{SO}_3\text{Ph})_2 \cdot \text{CO}_2\text{H}$ , similarly prepared from gallic acid, crystallises from acetic acid and melts at 200—208°. By the action of benzenesulphonic chloride on *p*-aminophenol, the compounds  $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$  and  $\text{SO}_3\text{Ph} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$  are obtained. The former melts at 150—152° and the latter at 125—126°. *o*-Aminophenol yields only the disubstituted product which forms reddish crystals and melts at 81—83°. From diaminophenol, two compounds probably of the composition  $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_3(\text{NH} \cdot \text{SO}_2\text{Ph}) \cdot \text{N}(\text{SO}_2\text{Ph})_2$  and  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NH} \cdot \text{SO}_2\text{Ph}) \cdot \text{N}(\text{SO}_2\text{Ph})_2$  respectively are formed. The compound,  $\text{SO}_3\text{Ph} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ , prepared from  $\beta$ -aminonaphthol, melts at 118—119°.

E. W. W.

**Hydrindene and a New Hydroxyhydrindene.** By J. MOSCHNER (*Ber.*, 1900, 33, 737—744).—The mother liquors from the crystallisation of pseudocumenesulphonic acid prepared from crude cumene, contain hydrindenesulphonic acid, the sodium salt of which crystallises in well-developed prisms containing  $3\text{H}_2\text{O}$ . Occasionally, solutions of this salt deposit the needle-shaped, efflorescent crystals containing  $4\text{H}_2\text{O}$  which were described by Krämer and Spilker (*Abstr.*, 1891, 205).

When fused with potassium hydroxide, the sodium sulphate yields 5-hydroxyhydrindene,  $\text{C}_9\text{H}_{10}\text{O}$ , which crystallises in white needles melting at 55°, and boils at 255° (corr.). Ferric chloride produces a faint bluish coloration. 5-Methoxyhydrindene,  $\text{C}_9\text{H}_9\text{OMe}$ , boils at 233—234° (corr.), and the ethoxy-compound at 246° (corr.). The methoxy-compound is converted by oxidation with very dilute nitric acid into 4-methoxyphthalic acid, which on hydrolysis yields 4-hydroxyphthalic acid, the constitution of the hydroxyhydrindene being thus established.

For the sake of comparison, 3- and 4-methoxyphthalic acids were prepared from compounds of known constitution. 3-Methoxy-*o*-xylene,

which melts at  $29^{\circ}$  and boils at  $199^{\circ}$  (corr.), is converted by oxidation into 3-methoxyphthalic acid, which on hydrolysis yields 3-hydroxyphthalic acid. 3-Ethoxy-o-xylene melts at  $10^{\circ}$  and boils at  $212.5^{\circ}$  (corr.). 4-Methoxy-o-xylene boils at  $204\text{--}205^{\circ}$  (corr.), and 4-ethoxy-o-xylene at  $218^{\circ}$  (corr.); the methoxyxylene is converted by oxidation into 4-methoxyphthalic acid.

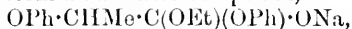
Sodium hydrindenesulphonate is converted by oxidation with potassium permanganate into 4-sulphophthalic acid, which when fused with potash yields 4-hydroxyphthalic acid, a small amount of hydroxybenzoic acid being formed at the same time.

A. H.

**Melting Point of Ethyl Formylphenylacetate.** By C. G. L. WOLF (*J. Physical Chem.*, 1900, 4, 123—129. Compare Abstr., 1896, i, 552).—By prolonged heating in baths maintained at a constant temperature, the author finds that fusion of ethyl formylphenylacetate will occur at any point above  $50^{\circ}$ , which is hence the stable triple point. By heating at  $100^{\circ}$  for some time and then cooling rapidly to  $-80^{\circ}$ , a glassy mass was obtained which liquefied at the ordinary temperature, and deposited crystals of the formyl compound in about 24 hours, so that crystallisation was hastened by the cooling. The probable form of the equilibrium diagram is given.

L. M. J.

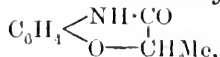
**Formation of Chains. XLII. Phenoxypropionic Acids and Derivatives.** By CARL A. BISCHOFF (*Ber.*, 1900, 33, 924—931).—Sodium phenoxide condenses with ethyl  $\alpha$ -bromopropionate at  $160^{\circ}$  to form ethyl  $\alpha$ -phenoxypropionic acid (Saarbach, Abstr., 1880, 392); neither phenol nor phenetole is produced.  $\alpha$ -Phenoxypropionyl-p-phenetide,  $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , crystallises from alcohol in colourless needles and melts at  $119^{\circ}$ . Sodium phenoxide and ethyl phenoxypropionate form an *additive* compound,



which decomposes when heated in a vacuum at  $190^{\circ}$ .

$\beta$ -Phenoxypropionic acid,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by the action of sodium phenoxide on  $\beta$ -iodopropionic acid, forms glistening crystals, melts at  $97.5\text{--}98^{\circ}$ , and does not give acrylic acid when heated. The affinity constant  $K$  is 0.0775 for the  $\alpha$ - and 0.0054 for the  $\beta$ -acid.

The nitration of  $\alpha$ -phenoxypropionic acid gives a mixture of *o*-nitrophenoxypropionic acid (m. p.  $157\text{--}159^{\circ}$ ) and *p*-nitrophenoxypropionic acid (m. p.  $141\text{--}142^{\circ}$ ), but these cannot be separated in a pure state by this method. By reduction with iron powder and acetic acid, the ortho-acid is converted into  $\alpha$ -methylpheno- $\beta$ -morpholone,



which separates from boiling water in colourless, glistening crystals and melts at  $144\text{--}145^{\circ}$ , whilst the para-acid is converted into  $\alpha$ -p-aminophenoxypropionic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , which crystallises from hot water in needles, and melts at  $219^{\circ}$ . T. M. L.

**Formation of Chains. XLIII.  $\alpha$ -Phenoxy butyric, -isobutyric, and -isovaleric Acids and their Esters.** By CARL A. BISCHOFF (*Ber.*, 1900, 33, 931—939).— $\alpha$ -Phenoxybutyric acid (Luchmann, Abstr.,

1896, i, 544) can be prepared by the condensation of ethyl  $\alpha$ -bromobutyrate with the theoretical quantity of sodium phenoxide, and hydrolysis of the ester with aqueous potassium hydroxide; it crystallises from light petroleum in eight-sided tablets, melts at  $82-83^\circ$  (Luchmann, 96—99°), boils at  $258^\circ$  without any separation of phenol, and has an affinity constant  $K=0.0682$ .

*Ethyl  $\alpha$ -phenoxyisobutyrate* boils at  $160-165^\circ$  under 7 mm. pressure. The acid,  $\text{OPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , crystallises from dilute alcohol in colourless needles, melts at  $97.5-98.2^\circ$ , has an affinity constant  $K=0.0434$ , and is completely decomposed on distillation into phenol and  $\alpha$ -methylacrylic acid. On nitration, the chief product appears to be  $\alpha$ -o-nitrophenoxyisobutyric acid, and on reducing the crude nitration product with iron powder and acetic acid no *p*-amino-acid could be isolated; the chief product of the reduction is *dimethylphenomorpholone*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CMe}_2 \\ \diagdown \quad \diagup \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$ , which crystallises from ether in colourless leaflets and melts at  $161.5^\circ$ .

*$\alpha$ -Phenoxyisovaleric acid*,  $\text{OPh}\cdot\text{CH}(\text{CHMe}_2)\cdot\text{CO}_2\text{H}$ , crystallises from light petroleum in long, silky needles, melts at  $81.5-82.3^\circ$ , has an affinity constant  $K=0.0466$ , and distils at  $250^\circ$  with formation of a trace of phenol. T. M. L.

**Crystalline Form of Indigotin.** By P. KLEY (*Rec. Trav. Chim.*, 1900, 19, 12—16).—Crystals of indigotin obtained by sublimation were imbedded in elder pith and cut into sections; microscopic examination of these showed that the crystals belong to the rhombic system, the following faces being commonly exhibited,  $\infty P$ ,  $\infty \bar{P}\infty$ ,  $mP\infty$ ,  $m\bar{P}\infty$ . Indigo also separates from boiling aniline solutions in rhombic crystals showing the following faces,  $\infty P$ ,  $OP$ ,  $\infty \bar{P}\infty$ ,  $m\bar{P}\infty$ . The crystals are markedly dichroic and in some cases contain rectangular cavities; the angle of extinction is  $0^\circ$ . Indirubin also crystallises in forms belonging to the rhombic system. G. T. M.

**Ethyl Fluoreneoxalate and Indeneoxalate.** By WILHELM WISLICENUS (*Ber.*, 1900, 33, 771—773. Compare Thiele, this vol., i, 298).—

*Ethyl fluoreneoxalate*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ , is prepared by leaving ethyl oxalate in contact with fluorene and sodium ethoxide in benzene solution for several hours at the ordinary temperature, and subsequently decomposing the crystalline sodium derivative with dilute sulphuric acid; it crystallises from benzene on adding light petroleum in lustrous, intensely yellow needles, melts at  $74-76^\circ$ , and with phenylhydrazine yields initially an *additive* compound, which melts at  $125^\circ$ , decomposes at  $140^\circ$ , and is transformed by crystallisation from glacial acetic acid into the yellow *phenylhydrazone*,  $\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_2$ , melting at  $150-151^\circ$ . *Fluoreneoxalic acid*,  $\text{C}_{13}\text{H}_9\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , obtained by hydrolysing its ethyl salt, melts, when *slowly* heated, at  $159-160^\circ$ .

*Ethyl indeneoxalate*,  $\text{CH}\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ , prepared in the



same way as ethyl fluorenoxalate, melts at about  $80^{\circ}$ , and cannot readily be purified owing to its crystallising with difficulty.

W. A. D.

**Condensation Products of Indene and Fluorene.** By JOHANNES THIRLE (*Ber.*, 1900, 33, 851—853. Compare preceding abstract). — Ethyl indeneoxalate,  $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$  or

$\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CO}_2\text{Et}$ , crystallises from light petroleum in orange-red needles and melts at  $85^{\circ}$ . From the mother liquors of the compound melting at  $135^{\circ}$ , obtained by Marekwald (*Abstr.*, 1895, i, 535) from the interaction of indene with benzaldehyde, a compound can be isolated, which forms orange-red, nodular crystals, melts at  $87^{\circ}$ , and is possibly benzylideneindene. *Benzylidenefluorene* (*phenyl-*

*diphenylene-ethylene*),  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{CHPh}$ , obtained by the sodium ethoxide condensation of benzaldehyde with fluorene in alcoholic solution, crystallises from alcohol in lustrous, white leaflets and melts at  $76^{\circ}$ .

W. A. D.

**Condensation of Benzyl Cyanide and Ethyl Fumarate.** By MARTIN HENZE (*Ber.*, 1900, 33, 966—971).—Ethyl fumarate (1 mol.) is added to a mixture of benzyl cyanide (2 mols.), sodium ethoxide (2 mols.), and absolute alcohol, and the whole warmed for 1—2 hours on the water-bath; the crude product is warmed with excess of sodium carbonate solution for some time on the water-bath, and when cold a *monosodium* salt separates as a sparingly soluble powder, which crystallises from water in glistening plates or needles. When treated with dilute sodium hydroxide, it dissolves, but in a few minutes crystals of a *disodium* salt are deposited; this separates from alcohol in colourless needles and is much more readily soluble in water than the monosodium salt. Carbon dioxide precipitates the monosodium salt from aqueous solution of the disodium salt and dilute mineral acids precipitate a *lactone*, melting at  $204$ — $205^{\circ}$ , for which the constitution  $\text{O} \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CPh}(\text{CN}) \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CN}$ , is suggested; this is readily soluble in most organic solvents with the exception of ether and light petroleum. The *methyl* ester, obtained by heating the monosodium salt with methyl alcohol and methyl iodide, crystallises in glistening plates melting at  $156^{\circ}$ , and is readily hydrolysed by sodium hydroxide or carbonate. The *oxime* crystallises in needles, melts and decomposes at  $179$ — $180^{\circ}$ , and although the compound contains a nitrile group, is not to be regarded as an amidoxime.

An acid which softens at  $105^{\circ}$  and is completely fused at  $115^{\circ}$  has also been isolated from the original condensation product. J. J. S.

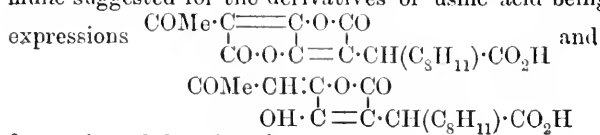
**Usnic Acid.** By OSKAR WIDMAN (*Annalen*, 1900, 310, 265—301. Compare this vol., i, 235).—Decarbusnic acid is the name by which Paternò originally indicated the compound  $\text{C}_{17}\text{H}_{18}\text{O}_7$ , obtained when usnic acid,  $\text{C}_{18}\text{H}_{16}\text{O}_7$ , is heated with alcohol at  $150^{\circ}$ ; the discoverer subsequently referred to this substance as decarbusnein (Paternò,

Abstr., 1882, 1080), but the present author points out that the original name is more suitable. The acid is optically inactive, and is dibasic; it crystallises from alcohol in long, yellowish needles, and melts at 176—177°. Alkaline solutions become red, and finally brown, when exposed to air, and reduce alkaline solutions of copper and silver salts when heated; potassium permanganate oxidises the substance instantaneously. The acetyl derivative,  $C_{17}H_{17}O_5 \cdot OAc$ , crystallises from methyl alcohol in small needles and melts at 120—121° (compare Hesse, Abstr., 1895, i, 299); an alcoholic solution develops a dark brownish-red coloration with ferric chloride. The *oxime anhydride*,  $C_{17}H_{17}O_5N$ , obtained by heating decarbusnic acid with a solution of hydroxylamine acetate in alcohol, crystallises in long, white, slender needles and melts at 214°; it dissolves readily in cold sodium hydroxide, becoming green, and finally dark brown, when exposed to air, the alcoholic solution developing a greenish-black coloration with ferric chloride. The *acetyl* derivative,  $C_{19}H_{19}O_6N$ , prepared by the action of boiling acetic anhydride on the oxime anhydride, crystallises from methyl alcohol in small, colourless needles which melt at 142°; it is insoluble in cold sodium hydroxide, and develops a green coloration when the alcoholic solution is treated with ferric chloride. The *phenylhydrazine* derivative,  $C_{29}H_{28}O_3N_4$ , prepared from alcoholic decarbusnic acid, phenylhydrazine, and acetic acid, crystallises in minute leaflets and melts at 210°; the production of this substance, which is insoluble in cold aqueous potash, involves addition of 2 mols. of phenylhydrazine with elimination of 3 mols. of water. The *compound*,  $C_{17}H_{20}O_5N_2$ , obtained on heating an alcoholic solution of decarbusnic acid with semicarbazide hydrochloride, melts at 237°, and becomes black when the solution in alcohol is treated with ferric chloride. The *anilide*,  $C_{23}H_{23}O_5N$ , crystallises from alcohol in long, slender, white needles, and melts at 235°; it dissolves slowly in cold potassium hydroxide.

*iso-Decarbusnic acid*,  $C_{17}H_{18}O_6$ , occurring as a bye-product in the preparation of decarbusnic acid, crystallises from alcohol in flat needles and melts at 197°; it is optically inactive, and the alcoholic solution becomes violet black when treated with ferric chloride. The acid dissolves very readily in sodium hydroxide, forming a yellow solution which darkens when exposed to air; potassium permanganate oxidises the liquid immediately.

*Usnic acid*,  $C_{18}H_{16}O_8$ , a dibasic acid obtained by incompletely oxidising usnic acid with potassium permanganate, crystallises from glacial acetic acid in yellow, rhomboidal plates, which become red at about 160°, and subsequently decompose and evolve gas; the alcoholic solution develops a brown coloration with ferric chloride, and solutions of the alkali salts are yellow or reddish-yellow. The acid is very unstable, and crystalline derivatives have not yet been obtained.

A theoretical discussion brings the paper to a conclusion, the formulæ suggested for the derivatives of usnic acid being based on the



for usnic and decarbusnic acids respectively.

M. O. F.

Attempts to obtain Active Isomerides of Hexahydro- and Isohexahydro-mellitic Acids. By PIO DE STEFANI (*Gazzetta*, 1900, 30, i, 187).—Hexahydromellitic acid, which is regarded by the author as a possible racemic compound, is not resolved into optically active components by either *Penicillium glaucum* or *Aspergillus glaucus*, nor is isohexahydromellitic acid acted on by *Penicillium* or *Mucor mucedo*.

T. H. P.

Friedel and Crafts' Reaction. By J. BOESEKEN (*Rec. Trav. Chim.*, 1900, 19, 19—26).—In the synthesis of aromatic ketones and sulphones by means of Friedel and Crafts' reaction, the condensation takes place in three stages: (1)  $R \cdot COCl + AlCl_3 = R \cdot COCl, AlCl_3$ ; (2)  $R \cdot COCl, AlCl_3 + HR' = R \cdot COR', AlCl_3 + HCl$ ; (3)  $R \cdot COR', AlCl_3 + nH_2O = R \cdot COR' + AlCl_3 \cdot nH_2O$ , where  $HR'$  represents an aromatic hydrocarbon or one of its derivatives (compare Perrier, this vol., i, 331).

Compounds of the type  $R \cdot COCl, AlCl_3$  have been obtained with benzoyl chloride, its *m*- and *p*-nitro-derivatives, and benzenesulphonic chloride. When these substances are treated with benzene, toluene, or anisole, compounds of the type  $R \cdot COR', AlCl_3$  are produced; the following are described:  $COPh_2, AlCl_3$ ,  $COPh \cdot C_6H_4Me, AlCl_3$ ,  $COPh \cdot C_6H_4OMe, AlCl_3$  and the corresponding *m*- and *p*-nitro-derivatives,  $NO_2 \cdot C_6H_4 \cdot COR, AlCl_3$ ,  $SO_2Ph_2, AlCl_3$ ,  $SO_2Ph \cdot C_6H_4Me, AlCl_3$ , and  $SO_2Ph \cdot C_6H_4OMe, AlCl_3$ . By boiling these compounds of the second type with 80 per cent. alcohol, the ketones and sulphones are obtained in a state of purity.

The sulphone,  $SO_2Ph \cdot C_6H_4OMe$ , melts at  $81^\circ$ .

G. T. M.

Alkylation of Ketones. By JOHN U. NEF (*Annalen*, 1900, 310, 316—335. Compare this vol., i, 4).—The author's explanation of the mechanism of such changes as the methylation of ammonia, ethyl sodiomalonate, and the cyanides, involves the assumption that the alkyl haloid undergoes dissociation into halogen hydride and a substituted methylene, which is then added to the substance under treatment (compare *loc. cit.*); the production of ethers during the action depends on the presence of an alcohol, and the preponderance of ether-formation over the first-named change is a question of the relative powers of dissociation displayed by the two competing substances. In presence of alcohol, ketones are indifferent towards alkyl haloids, but the author has found that when heated with methyl iodide and powdered potassium hydroxide, ketones readily undergo methylation. Acetophenone, for instance, yields phenyl ethyl ketone, phenyl *iso*-propyl ketone, and phenyl *tert*-butyl ketone, whilst phenyl ethyl ketone gives rise to phenyl *isopropyl* ketone.

Attempts to methylate phenyl *tert*-butyl ketone were fruitless, because the action of potash at  $160^\circ$  during 10 hours resolves the substance into benzene and trimethylacetic acid; the *oxime* crystallises from alcohol in flat, lustrous needles melting at  $165^\circ$ , and the *phenylhydrazone* crystallises in colourless needles and melts at  $92^\circ$ .

*Dibenzylacetophenone*,  $COPh \cdot CH(CH_2Ph)_2$ , prepared by heating acetophenone with benzyl chloride and potassium hydroxide at  $160$ — $170^\circ$ , crystallises in colourless needles melting at  $78^\circ$ , and boils at  $240$ — $250^\circ$  under 18 mm. pressure.

Methylation of acetone under the conditions described gives rise to

methyl ethyl ketone, methyl isopropyl ketone, diethyl ketone, and a small proportion of ethyl isopropyl ketone; further action of methyl iodide on these compounds yields methyl *tert*-butyl ketone (pinacolone) and diisopropyl ketone. *iso-Propyl butyl ketone* (pentamethylacetone),  $\text{COPr} \cdot \text{CMe}_3$ , prepared by heating pinacolone with methyl iodide and potassium hydroxide at  $130\text{--}140^\circ$ , boils at  $134^\circ$ . The *oxime* crystallises from dilute alcohol in lustrous leaflets melting at  $140^\circ$ , and is extremely volatile; the isomeric *amide*, which melts at  $115^\circ$ , is the result of a Beckmann transformation.

*Phenylmethylacetylene*,  $\text{CPh}:\text{CMe}$ , obtained by heating phenylacetylene with methyl iodide and potassium hydroxide, boils at  $74\text{--}75^\circ$  under 14 mm. pressure, and at  $181\text{--}182^\circ$  under atmospheric pressure.

The decomposition of the calcium salts of certain aliphatic acids on distillation is discussed from the point of view of the author's dissociation hypothesis. M. O. F.

**Ketoximes.** By PAVEL IW. PETRENKO-KRITSCHENKO and P. KASANEZKY (*Ber.*, 1900, 33, 854—856. Compare Abstr., 1899, i, 706).—Other oximes besides the one already investigated (*loc. cit.*) form double compounds with certain solvents.

$\beta$ -Benzildioxime crystallises with ethylene glycol ( $1\frac{1}{2}$  mols.), glycerol ( $\frac{1}{2}$  mol.), benzene (1 mol.), acetic acid ( $1\frac{1}{2}$  mols.), aniline (2 mols.), pyridine (2 mols.), and acetone (1 mol.).

The oxime of ketohydroxytriphenyltetrahydrobenzene (Smith, Abstr., 1893, i, 219) crystallises with alcohol (1 mol.), glycerol ( $1\frac{1}{2}$  mols.), acetic acid (3 mols.), aniline (2 mols.), and acetone (3 mols.).

Diacetyldioxime crystallises with pyridine (2 mols.) and ethylene glycol ( $\frac{1}{2}$  mol.).

The double compounds with organic substances having a high boiling point usually melt at a lower temperature than the oxime itself; the derivatives of more volatile liquids dissociate before the melting point of the oxime is reached. M. O. F.

**Anthraphenones.** By GUSTAVE PERRIER (*Ber.*, 1900, 33, 816).—In addition to the anthraphenone melting at  $143^\circ$  (Lippmann and Fleissner, Abstr., 1899, i, 918, give  $138^\circ$ ), obtained by the action of benzoyl chloride on anthracene in presence of aluminium chloride, an isomeride crystallising in white, lustrous needles and melting at  $75^\circ$  is also formed (compare *Thesis*, Paris, 1896), together with a third *isomeride* which forms small, white plates and melts at  $203^\circ$ .

W. A. D.

**Action of Menthol on Ethyl Acetoacetate.** By PAUL COHN (*Monatsh.*, 1900, 21, 200—204).—Menthol and ethyl acetoacetate, when heated at  $140\text{--}150^\circ$  for 4 hours, condense with the formation of *menthyl acetoacetate*, which crystallises in needles melting at  $30\text{--}32^\circ$ , boils at  $145^\circ$  under 11 mm. pressure, and has a specific rotation  $[\alpha]_D - 56.60^\circ$ . It yields a *phenylhydrazide*,  $\text{N}_2\text{HPh} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$ , which forms yellowish crystals melting between  $81^\circ$  and  $83^\circ$ .

R. H. P.

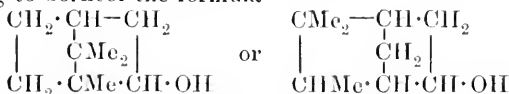
**Menthyl Acetoacetate.** By PAUL COHN and SIEGFRIED TAUSS (*Ber.*, 1900, 33, 731—734. Compare preceding abstract).—Menthyl

acetoacetate readily yields a phenylhydrazide, which crystallises in monoclinic tablets melting at 82—83° and decomposes spontaneously after a few days. Both menthyl acetoacetate and the hydrazide have a similar physiological action to menthol itself, whilst neither of them is a strong antiseptic. Menthyl acetoacetate readily yields a *cyanhydrin*,  $C_{15}H_{25}O_3N$ , which crystallises, with  $1H_2O$ , in lustrous needles. The *sodium* salt of the ester is a white, deliquescent mass, which readily reacts with alkyl iodides, but does not yield pure products.

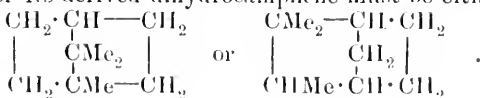
## A. II.

**Borneol and *iso*-Borneol.** By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 774—778).—*iso*-Borneol, on being heated with zinc dust for half an hour at 220°, yields a small quantity of camphene together with a larger proportion of a *dihydrocamphene* (*isodihydrocamphene*),  $C_{10}H_{18}$ , which crystallises from alcohol in fern-like aggregates belonging to the cubic system, melts at 85° and boils at 162° (uncorr.); borneol under similar conditions remains unchanged. It thus appears that *isoborneol* is a tertiary and borneol a secondary alcohol, since zinc dust is only capable of removing oxygen from tertiary alcohols (*Abstr.*, 1894, i, 611); the view that borneol and *isoborneol* are stereoisomerides must thus be rejected (compare Biltz, *Abstr.*, 1899, i, 297; Wagner, *Chem. Zeit.*, 1899, 930).

Pinene hydrochloride, which is now known to be the true chloride corresponding with borneol (compare Wagner and Brickner, this vol., i, 46), when reduced with sodium and alcohol, yields a *dihydrocamphene*,  $C_{10}H_{18}$ , which separates from alcohol in crystals belonging to the hexagonal system, melts at 155° and boils at 160—162° (uncorr.). Attributing to borneol the formula



the structure of its derived dihydrocamphene must be either



W. A. D.

**New Terpenoid Alcohol and its Derivatives.** By P. GENYRESSE (*Compt. rend.*, 1900, 130, 918—920).—*Pineuol*,  $C_{10}H_{16}O$ , obtained by passing nitrous fumes into cooled pinene, distilling the product in steam, and fractionating the distillate under ordinary and reduced pressures, is a pale yellow liquid having an agreeable odour; it boils at 225° under 740 mm., and at 143° under 38 mm. pressure; it has a sp. gr. 0.9952 at 0°, and index of refraction 1.497; its molecular refraction is 44.563; the theoretical value calculated from Brühl's data is 44.85, assuming the presence of one double linking in the molecule. The alcohol is insoluble in water but miscible in all proportions with the ordinary organic solvents; in chloroform solutions, it has  $[\alpha]_D -14.66^\circ$ . When distilled under ordinary pressures, pinenol is partly decomposed; it yields cymene on treatment with phosphoric oxide and combines with 1 mol. of bromine.

The *acetate* boils at  $150^{\circ}$  under 40 mm. pressure and has an odour resembling that of lavender.

*Pinenone*,  $C_{10}H_{14}O$ , resulting from the oxidation of pinenol with chromic acid mixture at the ordinary temperature, is a yellow liquid having an agreeable odour and boiling at  $132^{\circ}$  under 42 mm. pressure, it has a sp. gr. 0.9953 at  $0^{\circ}$ ,  $[\alpha]_D$  in chloroform solution  $-21.12^{\circ}$ , and an index of refraction 1.5002; its molecular refraction is 44.33, the calculated value, assuming the existence of one double linking, being 43.84. The ketone is insoluble in water but miscible in all proportions with the ordinary organic solvents; it combines with 1 mol. of bromine, and yields a *semicarbazone* melting at  $82^{\circ}$ .

*Pinenonoxime*,  $C_{10}H_{14}NOH$ , is prepared by heating the ketone with an alcoholic solution of hydroxylamine; a small quantity is also formed in the preparation of pinenol from pinene; in this experiment, it is, however, formed from pinenone, and not from the alcohol, since the latter does not yield the oxime on treatment with nitrous fumes. The compound crystallises in the orthorhombic system, melts at  $89^{\circ}$ , distils with partial decomposition at  $170^{\circ}$  under 40 mm. pressure, and has  $[\alpha]_D -22.3^{\circ}$ . It combines with bromine (1 mol.), forming the *dibromide*,  $C_{10}H_{14}Br_2NOH$ , melting at  $152^{\circ}$ ; the *phenyl carbimide*,  $C_{10}H_{14}NO \cdot CO \cdot NPh$ , crystallises in needles melting at  $135^{\circ}$ ; the *benzoyl* derivative,  $C_{10}H_{14}NOBz$ , crystallises from alcohol and melts at  $105^{\circ}$ , and the *butyryl* derivative melts at  $74^{\circ}$ . G. T. M.

**Conversion of Carvone into Limonene.** By L. TSCHÜGAEFF (*Ber.*, 1900, 33, 735—736).—Dihydrocarveol, prepared by the reduction of *d*-carvone, can readily be converted by the method previously described by the author (this vol., i, 129) into *methyl dihydrocarveylxanthate*,  $C_{10}H_{17}O \cdot CS_2Me$ , which is a thick, yellow oil. On distillation, this substance yields two hydrocarbons, one boiling at  $172-173.5^{\circ}$ , and the other at  $174-176^{\circ}$ . With bromine, the latter yields limonene tetrabromide, which, by the action of zinc dust on the alcoholic solution, is converted into pure *d*-limonene. The hydrocarbon of lower boiling point is more strongly dextrorotatory than limonene, and appears not to yield a crystalline tetrabromide; its nature is being investigated. A. H.

**Preparation of Camphene and Menthene from the Corresponding Alcohols.** By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 76—77).—Camphene is readily obtained from borneol by heating with sulphuric acid, diluted with double its volume of water, at a temperature of  $60-100^{\circ}$  for 6 to 8 hours; in the same way, menthene may be prepared from menthol. The yield of hydrocarbon is in each case about 90 per cent. of the theoretical. This method may be used for obtaining other hydrocarbons, and also for preparing methylcyclohexamethylene ketone from pulegone.

T. H. P.

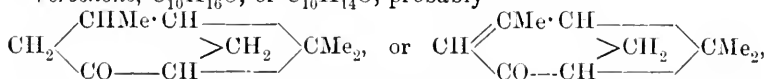
**Essence of Chrysanthemum.** By GUSTAVE PERRIER (*Bull. Soc. Chim.*, 1900, [iii], 23, 216—217).—The green leaves of *Chrysanthemum Japonicum*, when distilled with water, yield about 0.16 per cent. of a greenish, somewhat oily liquid, having an odour recalling

mint and camomile, which boils at  $160^{\circ}$ , and has a sp. gr. 0.932 at  $15^{\circ}$  and refractive index 1.4931 at  $18^{\circ}$ . It is almost insoluble in 70 per cent., but soluble in 10 parts of 95 per cent., alcohol; when cooled to  $-15^{\circ}$ , it deposits a small quantity of an amorphous solid, probably a paraffin, and at a still lower temperature it completely solidifies. The essence has an acid reaction, partially combines with sodium hydrogen sulphite, and has a saponification number 8.61; the products of hydrolysis seem to include angelic acid. N. L.

**The Aldehydic Constituents of Oil of Verbena.** Verbenone. By MAX KERSCHBAUM (*Ber.*, 1900, 33, 885—893).—A sample of oil of verbenone, of sp. gr. 0.903 at  $17^{\circ}$ , and having  $\alpha_D -12^{\circ}30'$ , obtained from Grasse, was found to contain 26 per cent. of citral and 74 of terpenes and alcohols; the citral contained 17—20 per cent. of citral *b* in addition to citral *a* (compare Tiemann, *Abstr.*, 1899, i, 250). No transformation of the citral takes place, as Barbier supposes (*Abstr.*, 1899, i, 769), when it is converted into the hydrosulphonic acid.

Another sample, of Spanish origin, had a sp. gr. 0.926 at  $17^{\circ}$ , and  $\alpha_D +2^{\circ}45'$ . This was shaken with aqueous sodium sulphite and hydrogen carbonate, the solution extracted repeatedly with ether, and then decomposed with sodium hydroxide. The regenerated aldehyde, &c., was shaken with alkaline cyanoacetic acid solution until it dissolved, and the solution extracted repeatedly with ether. The product so obtained is a ketone, and has been named *verbenone*. The oil contained 13 per cent. of citral, 1 of verbenone, and 86 of alcohols and terpenes; the citral contained 18—20 per cent. of citral *b*.

*Verbenone*,  $C_{10}H_{16}O$ , or  $C_{10}H_{14}O$ , probably



is a colourless oil with an odour suggestive of camphor and peppermint; it boils at  $103-104^{\circ}$  under 16 mm. pressure, has a sp. gr. 0.974 at  $17^{\circ}$ , index of refraction  $n_D$  1.49951, and rotation  $\alpha_D +66^{\circ}$ ; its *semicarbazone* melts at  $208-209^{\circ}$ . It decolorises permanganate at once, but not bromine in acetic acid solution; it is not affected by alkalis, and does not condense with acetone. When oxidised with permanganate, at  $0^{\circ}$ , at starting it yields a very little acetone, but the main product

is a *ketonic acid*,  $C_9H_{14}O_3$ , probably  $CO_2H \cdot CH \begin{array}{c} \diagup CMe_2 \\ \diagdown CH_2 \end{array} CH \cdot COMe$ ,

which melts at  $127-128^{\circ}$ , does not decolorise bromine, and decolorises permanganate only when heated; its *semicarbazone* melts at  $212^{\circ}$ . When treated with alkaline hypobromite, this acid yields bromoform and an acid,  $C_8H_{12}O_4$ , identical with Baeyer's norpic acid (*Abstr.*, 1896, i, 621); when evaporated with acetyl chloride and then heated with aniline, it yields an *anilic acid*,  $C_{14}H_{17}O_3N$ , which melts at  $212-213^{\circ}$ . C. F. B.

**India-rubber.** By CARL OTTO WEBER (*Ber.*, 1900, 33, 779—796, and *J. Soc. Chem. Ind.*, 1900, 19, 215—221).—In agreement with Gladstone and Hibbert (*Trans.*, 1888, 53, 679), the author finds that

Para rubber contains but a small quantity (about 6.5 per cent.) of material insoluble in chloroform; this has a fibrous structure and swells enormously, but without dissolving, in contact with chloroform, ether, light petroleum, or carbon disulphide, and has the composition  $C_{30}H_{64}O_{10}$ , which suggests a possible relationship with Spiller's resin,  $C_{20}H_{48}O_{10}$ , obtained by the oxidation of india-rubber (this Journal, 1865, 3, 44), although the author considers it to be rather a "link between india-rubber and the carbohydrates" than a transformation product of the former. Its composition, however, closely approximates to that of a polyprene hydrate,  $C_{30}H_{48} \cdot 10H_2O$ . Gladstone and Hibbert's view that it is formed by the action of heat on the india-rubber juice during drying does not appear to be justified; other varieties of india-rubber (Congo-ball, Lagos, Borneo, and Assam) do not contain a portion insoluble in chloroform.

On adding alcohol to the chloroform solution of Para rubber, a precipitate is obtained which, after drying in an atmosphere free from oxygen, has the composition  $(C_{10}H_{16})_n$ . The same hydrocarbon (polyprene) apparently exists in all varieties of india-rubber, although these contain in addition slightly differing amounts of oxygenated impurities; in all samples, however, the atomic ratio  $C:H=10:16$  approximately.

The tetrabromide,  $C_{10}H_{16}Br_4$ , formed by the action of bromine on polyprene dissolved in chloroform, is obtained as a snow-white mass by pouring the solution into alcohol, and thus prepared, can, after drying, be kept for an indefinite period without decomposing, although Gladstone and Hibbert have stated that it is unstable, rapidly losing hydrogen bromide. It is insoluble in all solvents except chloroform, and even with the latter its solubility varies; it is remarkable that, when recovered chloroform is used in the preparation, the product obtained, although not differing in composition from other samples, is completely insoluble in the solvent named. On the other hand, one preparation was found to be more soluble in benzene than in chloroform. It thus appears that polyprene tetrabromide is capable of undergoing complex physical change. Towards cold fuming nitric acid, and boiling solutions of chromic acid or of chromic and sulphuric acids, on the other hand, the substance is completely indifferent; when heated alone above  $50-60^\circ$ , hydrogen bromide is evolved, and a dark brown product obtained. On heating with alcoholic sodium ethoxide at  $120^\circ$ , part of the bromine appears to be replaced by ethoxyl.

Contrary to the usual statements, polyprene readily unites with iodine; after 12 hours action at the ordinary temperature in chloroform solution, a *product*,  $C_{20}H_{32}I_6$ , is obtained, which is insoluble in all solvents except warm aniline or toluidine, and is decomposed on heating at  $80^\circ$  or  $100^\circ$ .

Dry hydrogen chloride below  $10^\circ$  acts indefinitely on polyprene in chloroform solution, but when moist the *dihydrochloride*,  $C_{10}H_{18}Cl_2$ , is obtained; this is a white, friable mass, which is insoluble in nearly all solvents except chloroform, and on heating at  $40^\circ$ , loses hydrogen chloride until its composition approximates to  $C_{10}H_{17}Cl$ ; on raising the temperature, no further change takes place, so that the mono-



hydrochloride appears to be relatively stable. All attempts to prepare corresponding hydrobromides or hydriodides ended in failure; and the same holds true of all attempts to determine the molecular weight of the substances hitherto described.

On heating polyprene tetrabromide with phenol at  $100^{\circ}$ , it changes from white to green, then successively through dull grey, dark blue, to purple or crimson, and finally dissolves with evolution of hydrogen bromide; on completing the action by heating for 10 minutes at  $150^{\circ}$ , a buff-coloured, pulverulent substance having the composition of a *polyprene tetraphenoxide*,  $C_{10}H_{16}(OPh)_4$ , can be isolated, the yield corresponding with 50 per cent. of the tetrabromide employed; it is readily soluble in aqueous and alcoholic sodium hydroxide, alcohol, acetone, ether, and ethyl acetate, but insoluble in benzene, chloroform, carbon bisulphide, and light petroleum. By limiting the temperature of the action to from  $90$ — $95^{\circ}$ , and varying the method of isolating the product, substances are obtained which differ in colour from dull crimson to a rich shade of indigo, and correspond in composition with either *dioxypolyprene tetraphenoxide*,  $C_{10}H_{16}O_2(OPh)_4$ , or with the compound  $C_{10}H_{16}O_5(OPh)_5$ ; under one set of conditions, the same product is always obtained. On prolonged boiling with aqueous sodium hydroxide, all these substances lose phenol and yield products containing an increasing number of hydroxyl groups.

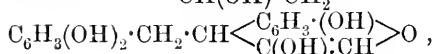
A large number of other aromatic hydroxy-compounds behave like phenol with polyprene tetrabromide, but phenol-ethers are without action.  
W. A. D.

**Sugars of some Glucosides.** By EMIL VOTOČEK (*Zeit. Zuck.-ind. Böhm.*, 1900, 24, 239—248).—A number of glucosides have been examined to ascertain whether the sugars they yield are hexoses or methylpentoses, the method employed being distillation with 12 per cent. hydrochloric acid. With æsculin, arbutin, apiin, phloridzin, gratiolin, jalapin, ononin, syringin, neither furfuraldehyde nor methylfurfuraldehyde is obtained, showing that their sugars belong to the hexose group. Saponin and cyclamin give small quantities of furfuraldehyde, possibly owing to the presence of impurities, whilst with chinovin, hesperidin, and xanthorhamnin, the amounts of methylfurfuraldehyde obtained prove conclusively the presence of methylpentoses. In the case of convolvulin (rhodeoretin), the methylfurfuraldehyde formed corresponds with an amount of methylpentose equal to 40.6 per cent. of the glucoside, whilst solanin gives 19.6 per cent. of its weight of a methylpentose.  
T. H. P.

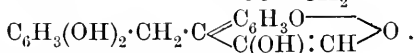
**Compounds from Rhubarb and Allied Substances.** By CARL LIEBERMANN (*Annalen*, 1900, 310, 364—369. Compare Hesse, this vol., i, 40).—A criticism of the constitutional formulæ employed by Hesse in representing chrysophanic acid, rhabarberone, protophyscion, rhein, and emodin (*loc. cit.*).  
M. O. F.

**Brazilin.** By STANISLAUS VON KOSTANECKI and W. FEUERSTEIN (*Chem. Centr.*, 1900, i, 605—606; from *Arch. Sci. phys. nat. Genève*, [iv], 8, 385—386).—When the diethyl ether of the product obtained

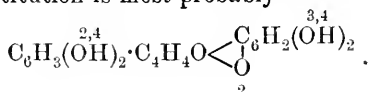
by Schall and Dralle by oxidising brazilin is heated with sodium ethoxide, fisetol diethyl ether,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OEt}$ , melting at  $42-44^\circ$ , and formic acid are formed. The composition of brazilin is probably  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{CH}(\text{OH})\cdot\text{CH}_2 \end{smallmatrix}\text{O}$  or



and of brazilein,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{CO}-\text{CH}_2 \end{smallmatrix}\text{O}$  or



Since hæmatoxylin does not yield Schall and Dralle's compound on oxidation, its constitution is most probably



E. W. W.

**Alkaloids of the Solanaceæ.** By JOHANNES GADAMER (*Annalen*, 1900, 310, 352—363. Compare Hesse, this vol., i, 50).—A detailed reply to the criticisms of Hesse respecting the author's investigations of atropine, hyoscyamine, hyoscyne, atroscine, and scopolamine.

M. O. F.

**Combination of Basic with Acidic Colouring Matters.** By ALPHONSE SEYEWETZ (*Compt. rend.*, 1900, 130, 842—844).—It is well known that many basic and acidic colouring matters have the property of combining to form insoluble compounds, but the author finds that similar results are not observed, as a rule, if one of the substances is a non-tinctorial basic or acidic derivative. Acids do not form insoluble compounds with auramine, and bases do not form insoluble compounds with ammonium picrate. Experiments with a large number of substances show that benzene derivatives containing an acidic group or several identical acidic groups such as  $\text{CO}_2\text{H}$ ,  $\text{OH}$ ,  $\text{SO}_3\text{H}$ ,  $\text{NO}_2$ ,  $\text{CO}\cdot\text{CO}$ , &c., do not form precipitates with auramine, but if such compounds contain two or more different groups, they precipitate it. Derivatives containing only one carboxyl and one hydroxyl group are exceptions to this rule, and the introduction of a third group is necessary before insoluble compounds with auramine can be formed. Non-tinctorial amino-derivatives and compounds containing the groups  $\cdot\text{NH}$ ,  $\text{N}\cdot$ ,  $\cdot\text{N}\cdot\text{N}\cdot$ ,  $\text{ON}_2\cdot$ ,  $\cdot\text{NH}\cdot\text{NH}\cdot$ , or  $\begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$ , or nitrogen in the benzene, naphthalene, or anthracene nuclei do not form precipitates with ammonium picrate. Compounds containing both an amino-group and the diazo-group in the benzene nucleus at first sight seem to be exceptions to this rule, but they are themselves colouring matters. The introduction of a sulphonic group into an aromatic nucleus containing several amino-groups likewise confers on it the property of precipitating auramine.

It follows that the chromophore of the colouring matter plays an

important part in the reaction referred to, and that the formation of the insoluble products in question may be regarded as characteristic of colouring matters.

C. H. B.

**Action of Bromoform and Chloroform on some Pyrroles.** By O. Bocchi (*Gazzetta*, 1900, 30, i, 89—96).—3-Chloro-2:6-dimethylpyridine,  $C_7H_8NCl$ , prepared by the gradual addition of chloroform (1 mol.) to a solution of 2:5-dimethylpyrrole (1 mol.) in an alcoholic solution of sodium ethoxide (2 mols.), is a colourless liquid, heavier than water, in which it is appreciably soluble; its *hydrochloride* crystallises in colourless, deliquescent needles; the *picrate*,  $C_{13}H_{11}O_7N_4Cl$ , separates from water in aggregates of yellow needles melting at  $150-151^\circ$ ; the *aurichloride* crystallises in slender needles melting at  $131^\circ$ , and is soluble in very dilute hydrochloric acid; the *platinichloride* forms orange-yellow needles melting at  $212^\circ$ .

3-Bromo-2:6-dimethylpyridine,  $C_7H_8NBr$ , is prepared in like manner to the chloro-compound, and has similar properties. Its *hydrochloride* crystallises in colourless, deliquescent needles, and the *picrate* separates from methyl alcohol in long, yellow needles melting at  $148^\circ$ . On reduction with zinc and dilute hydrochloric acid, the bromo-base yields 2:6-dimethylpyridine.

Bromoform acts on 2:4-dimethylpyrrole in presence of sodium ethoxide, yielding a small quantity of a yellowish oil, which has an intense pyridic odour, and is completely soluble in acids. This oil consists mainly of two pyridine bases, as it gives two distinct *picrates*, which separate from methyl alcohol, the one in long needles melting at  $176^\circ$ , and the other in prisms melting at about  $170^\circ$ . The formation of two different bases is readily explained on theoretical grounds; the compounds were not investigated further, owing to the small yield.

T. H. P.

**Action of Amines on Dibromotriacetoneamine.** By HERMANN PAULY and CARL BOEHM (*Ber.*, 1900, 33, 919—923. Compare Pauly and Rossbach, *Abstr.*, 1899, i, 773).—The action of primary and secondary amines on dibromotriacetoneamine is similar to that of ammonia, but no definite substances could be isolated from the product of the action of tertiary or aromatic amines on the base.

By the action of methyl iodide on tetramethylpyrrolinecarboxylmethylamide (Pauly and Rossbach, *loc. cit.*), there is produced the hydriodide of a base which crystallises from light petroleum in long, silky needles, and melts at  $108-109^\circ$ ; the same base is also produced in small quantities by the action of methyl iodide on the potassium salt of N-methyltetramethylpyrrolinecarboxylamide, and it must therefore be represented by the formula

$$NMe \begin{array}{c} \diagup CMe_2 \cdot CH \\ \diagdown CMe_2 \cdot C \cdot CO \cdot NHMe \end{array}$$

The constitution of tetramethylpyrrolinecarboxylmethylamide has been established by hydrolysing it with fuming hydrochloric acid at  $130^\circ$ , when the hydrochlorides of tetramethylpyrrolinecarboxylic acid and methylamine are obtained.

*Tetramethylpyrrolinecarboxylbenzylamide*,  $C_8H_{14}N \cdot CO \cdot NH \cdot CH_2Ph$ , crystallises from water in small, rhombic tablets, and melts at  $71^\circ$ .

*Tetramethylpyrrolinecarboxyldimethylamide*,  $C_8H_{14}N \cdot CO \cdot NMe_2$ , boils at  $125^\circ$  under 15 mm. pressure, solidifies at  $45^\circ$  in radiating needles, and is hydrolysed by hydrochloric acid to the hydrochlorides of dimethylamine and the acid. *Tetramethylpyrrolinecarboxylpiperidide*,  $C_8H_{14}N \cdot CO \cdot NC_5H_{10}$ , boils at  $170^\circ$  under 19 mm. pressure, and solidifies at  $74^\circ$  in radiating needles. T. M. L.

**Action of the Sodium Alkyloxides on Ethyl Phthalylaminoacetate and its Homologues.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, **33**, 980—995).—The sodium alkyloxides do not hydrolyse ethyl phthalylaminoacetate, but convert it into derivatives of isoquinoline. Ethyl phthalylaminoacetate is converted by sodium ethoxide into *ethyl 4-hydroxyisocarbostyryl-3-carboxylate*,  $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{:} \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ , which crystallises in snow-white needles melting at  $194^\circ$ . Sodium methoxide produces a similar change, the corresponding *methyl ester* being formed in silky needles melting at  $221$ — $222^\circ$ . The *sodium* compound,  $C_{11}H_8O_4NNa$ , is a yellow, crystalline powder.

On treatment with hydrobromic acid, the methyl ester yields *4-hydroxyisocarbostyryl*,  $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{:} \text{CH} \end{smallmatrix}$ , which crystallises in needles, does not melt below  $250^\circ$ , and readily undergoes oxidation in alkaline solution (compare following abstract); it is converted by reduction with hydriodic acid into *isocarbostyryl*,  $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{CH} \text{:} \text{CH} \end{smallmatrix}$ . This substance yields, with phosphorus oxychloride, *1-chloroisoquinoline*,  $C_6H_4 \begin{smallmatrix} \text{CCl} \text{:} \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \text{:} \text{CH} \end{smallmatrix}$ , which melts at  $37$ — $38^\circ$  and boils at  $274$ — $275^\circ$ . The monochloroisoquinoline previously described must therefore be 3-chloroisoquinoline (Gabriel, *Abstr.*, 1887, 62).

Hydroxyisocarbostyryl is converted by phosphorus oxychloride into two compounds: 1 : 4-*Dichloroisoquinoline*,  $C_6H_4 \begin{smallmatrix} \text{CCl} \text{:} \text{N} \\ \diagup \quad \diagdown \\ \text{CCl} \text{:} \text{CH} \end{smallmatrix}$ , melting at  $88$ — $89^\circ$ , is formed in small quantity, whilst the chief product consists of 4-*hydroxy-1-chloroisoquinoline*,  $C_6H_4 \begin{smallmatrix} \text{CCl} \text{=} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{:} \text{CH} \end{smallmatrix}$ , which crystallises in long, silky needles melting at  $195$ — $196^\circ$ . This base is converted by methyl alcoholic potash into 4-*methoxy-1-chloroisoquinoline*,  $C_6H_4 \begin{smallmatrix} \text{CCl} \text{=} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OMe}) \text{:} \text{CH} \end{smallmatrix}$ , which forms a mass of radiating crystals and melts at  $77^\circ$ . Hydroxychloroisoquinoline is reduced by hydriodic acid and phosphorus to tetrahydroisoquinoline.

*Ethyl  $\alpha$ -phthalyliminopropionate*,  $C_8H_8O_3 \cdot N \cdot CHMe \cdot CO_2Et$ , is prepared by the action of potassium phthalimide on ethyl  $\alpha$ -bromopropionate, and forms colourless crystals melting at  $61$ — $63^\circ$ . Sodium methoxide converts it into 4-*hydroxy-3-methylisocarbostyryl*,

$C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{:} \text{C}Me \end{smallmatrix}$  +  $H_2O$ , which forms colourless crystals, loses its

water at  $200^{\circ}$ , and is a weak base, the hydrochloride being decomposed by water. The base is converted by ethyl iodide into 4-methoxy-3-methylisocarbostyryl, which crystallises in needles melting at  $195^{\circ}$ , and is insoluble in alkalis. Hydriodic acid converts methylhydroxyisocarbostyryl into 3-methylisocarbostyryl, whilst phosphorus oxychloride converts it into 1-chloro-4-hydroxy-3-methylisoquinoline,

$C_6H_4 \begin{smallmatrix} \text{CCl}=\text{N} \\ | \\ \text{C}(\text{OH})\text{:CMe} \end{smallmatrix}$ , which is a crystalline powder melting at  $163^{\circ}$ .

On methylation, this substance yields 1-chloro-3-methyl-4-methoxyisoquinoline,  $C_6H_4 \begin{smallmatrix} \text{CCl}=\text{N} \\ | \\ \text{C}(\text{OMe})\text{:CMe} \end{smallmatrix}$ , which melts at  $49^{\circ}$  and boils at  $302-304^{\circ}$ . Chlorohydroxymethylisoquinoline is converted by reduction

into 3-methyltetrahydroisoquinoline,  $C_6H_4 \begin{smallmatrix} \text{CH}_2\text{NH} \\ | \\ \text{CH}_2\text{:CHMe} \end{smallmatrix}$ , which boils at  $236-237^{\circ}$ , and with sodium nitrite yields a nitrosamine,  $C_{10}H_{12}N\cdot NO$ , crystallising in needles melting at  $77-78^{\circ}$ . In the preparation of chlorohydroxymethylisoquinoline, 1:4-dichloro-3-methylisoquinoline,  $C_6H_4 \begin{smallmatrix} \text{CCl:N} \\ | \\ \text{CCl:CMe} \end{smallmatrix}$ , is obtained in small quantity as

a hard, crystalline mass, which melts at  $95^{\circ}$ , boils at  $300-312^{\circ}$ , yields 3-methylisoquinoline on reduction with hydriodic acid, and is converted by sodium methoxide into 4-chloro-1-methoxy-3-methylisoquinoline,  $C_6H_4 \begin{smallmatrix} \text{C}(\text{OMe})\text{:N} \\ | \\ \text{CCl}=\text{CMe} \end{smallmatrix}$ , which crystallises in slender needles melting at  $57-58^{\circ}$ .

Ethyl  $\alpha$ -phthalyliminobutyrate,  $C_8H_4O_2N\cdot CH\text{Et}\cdot CO_2\text{Et}$ , boils at  $333-337^{\circ}$ , and is converted by sodium methoxide into 4-hydroxy-3-

ethylisocarbostyryl,  $C_6H_4 \begin{smallmatrix} \text{CO}=\text{NH} \\ | \\ \text{C}(\text{OH})\text{:CEt} \end{smallmatrix}$ , which crystallises in lustrous needles. The hydrochloride,  $C_{11}H_{11}O_2N\cdot HCl$ , is decomposed by water; hydriodic acid reduces it to 3-ethylisocarbostyryl.

Benzylphthalimide does not react in a similar manner to the phthalylaminoacetic ester, but is converted by sodium methoxide into benzylphthalamic acid. A. H.

**4-Hydroxyisocarbostyryl.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, 33, 996-1000. Compare the foregoing abstract).

—4-Hydroxyisocarbostyryl,  $C_6H_4 \begin{smallmatrix} \text{C}(\text{OH}) \\ | \\ \text{CO}\text{:NH} \end{smallmatrix} \text{CH}$ , resembles indoxyl in constitution, and, like the latter, readily undergoes oxidation, the product,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ | \\ \text{CO}\text{:NH} \end{smallmatrix} \text{C:C} \begin{smallmatrix} \text{CO} \\ | \\ \text{NH}\text{:CO} \end{smallmatrix} C_6H_4$ , termed by the author *carbindigo*, bearing to indigo the same relation as the original compound bears to indoxyl.

Carbindigo is formed from hydroxyisocarbostyryl by the action of ferric chloride on its acid solution, or by the spontaneous oxidation of its alkaline solution in the air. It is insoluble in the usual solvents, but crystallises from nitrobenzene in flat, ruby-red needles, which melt above  $400^{\circ}$ . It is converted by alkalis into a brown mass and dissolves in warm aqueous potash. It is reduced by alcoholic

ammonium sulphide to a yellow "leuco-compound,"  $C_{18}H_{12}O_4N_2$ , which is an insoluble, lemon-yellow, crystalline powder. On oxidation with fuming nitric acid, carbindigo yields *phthalonimide*,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{CO} \end{smallmatrix}$ , which melts and decomposes at  $198-220^\circ$ ; the formation of this substance is quite analogous to that of isatin from indigo. On hydrolysis, phthalonimide yields phthalonic acid and *phthalonamic acid*,  $NH_2 \cdot CO \cdot C_6H_4 \cdot CO \cdot CO_2H$ , which crystallises, with  $1\frac{1}{2}H_2O$ , in short, compact prisms and melts and decomposes at  $178-179^\circ$ . The *silver* salt crystallises in flat needles. Phthalonamic acid is converted by alkali hypochlorite into isatic acid, its constitution being thus established.

A. H.

**Synthesis of Indoline Bases.** By KARL BRUNNER (*Monatsh.*, 1900, 21, 156—183. Compare Abstr., 1898, i, 384 and 682).—The bases obtained by E. Fischer (*loc. cit.*) and analogous compounds are best represented by formulæ of the type,  $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{NPh} \end{smallmatrix} > C:CH_2$ , and the corresponding salts by  $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{NCIPh} \end{smallmatrix} > CMe$ .

1-Phenyl-3:3-dimethyl-2-methyleneindoline forms a *stannochloride*,  $C_{17}H_{17}N, HSnCl_3$ , which crystallises in lustrous, yellow tablets melting at  $121-122^\circ$ ; a *mercurichloride*, which melts at  $189^\circ$  to a violet mass; a *ferrichloride*, which forms small, yellow needles melting at  $162^\circ$ , and a *platinichloride* which melts at  $198^\circ$ .

1-Phenyl-3:3-dimethyl-2-indolinol is prepared by decomposing with potassium hydroxide the indefinite *tin* salt obtained by treating isobutylidenediphenylhydrazine with an alcoholic solution of stannous chloride; it crystallises from benzene with  $\frac{1}{4}C_6H_6$  in lustrous, colourless prisms, which melt between  $110^\circ$  and  $115^\circ$ , lose the benzene of crystallisation on keeping, and then melt at  $125^\circ$ ; it forms a *mercurichloride*,  $C_{16}H_{15}N, HHgCl_3$ , which melts and decomposes at  $124^\circ$ ; its solution in hydrochloric acid is a delicate reagent for nitrites, which produce a violet-blue coloration; oxidation in alkaline solution converts it into 1-phenyl-3:3-dimethyl-2-indolinone, which forms colourless crystals melting at  $72^\circ$  and boiling at  $210-212^\circ$  under 30 mm. pressure. On boiling a solution of 1-phenyl-3:3-dimethyl-2-indolinol with hydrochloric acid, it is converted into 1-phenyl-2:3-dimethylindole, which is a viscous, fluorescent oil boiling at  $228-230^\circ$  under 60 mm. pressure; this forms a *picrate* melting at  $131^\circ$ , and with methyl iodide yields the hydriodide of 1-phenyl-3:3-dimethyl-2-methyleneindoline.

R. H. P.

**Syntheses in the Acridine Series. I. 2'-Methyl-1:2-naphth-acridine.\*** By FRITZ ULLMANN and E. NAEF (*Ber.*, 1900, 33, 905—912).—When dihydroxydinaphthylmethane,  $CH_2(C_{10}H_6 \cdot OH)_2$ , the condensation product of formaldehyde with  $\beta$ -naphthol (Abel, Abstr., 1893, i, 172; Manasse, 1894, i, 577) is heated with a mixture of *p*-toluidine and its hydrochloride, eventually to  $200^\circ$ ,  $\beta$ -naphthol is obtained along with a dihydroacridine and an acridine, the last result-

\* The names assigned to the compounds described in these papers are misleading, as methyl-naphthacridine would have the formula  $C_{22}H_{15}N$ , not  $C_{18}H_{13}N$ .

ing from a partial oxidation of the leuco-compound by the oxygen of the air. The same result is obtained when either of the condensation products of formaldehyde with *p*-toluidine, methylenedi-*p*-tolylidimide (Eberhardt and Welter, Abstr., 1894, i, 451) or anhydroformaldehyde-*p*-toluidine, is heated with  $\beta$ -naphthol; and also when  $\beta$ -naphthol, *p*-toluidine and trioxymethylene (paraformaldehyde) are heated together.

"Methylnaphthacridine,"  $C_6H_4 \begin{array}{c} \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{CMe} \\ \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{N} - \text{C} \cdot \text{CH} \cdot \text{CH} \end{array}$ , melts at  $158^\circ$  and boils at  $460^\circ$ ; it is almost white, but the salts are yellow. These are comparatively little soluble in water; the *hydrochloride*, *nitrate*, and *picrate* were prepared (the base is a monoacid one); with 4 per cent. fuming sulphuric acid, it yields a pale yellow *monosulphonic acid*. "Methyldihydronaphthacridine,"  $C_{18}H_{15}N$ , is colourless and melts at  $190-193.5^\circ$ . C. F. B.

Syntheses in the Acridine Series. II. 2'-Methyl-3'-amino-1:2-naphthacridine. By FRITZ ULLMANN and E. NAEF (*Ber.*, 1900, 33, 912-919).—When *m*-tolylenediamine is treated with formaldehyde in neutral (aqueous or alcoholic) solution at the ordinary temperature, the product is anhydroformaldehyde-*m*-tolylenediamine,  $C_8H_{10}N_2$ , which melts between  $150^\circ$  and  $180^\circ$ ; formaldehyde can be obtained from it and detected by Tollens' method (this vol., i, 56), and so Schiff's view of its constitution (Abstr., 1891, 1258) is correct, not so that of Terisse (*Chem. Zeit*, 1899, 286). In dilute sulphuric acid solution at  $60^\circ$ , the product is tetraminoditolylmethane,  $CH_2[C_6H_2Me(NH_2)_2]_2$ , which melts at  $203-204^\circ$ .

When a mixture of *m*-tolylenediamine and its hydrochloride is heated with dihydroxydinaphthylmethane, when  $\beta$ -naphthol is heated with anhydroformaldehyde-*m*-tolylenediamine, or with tetraminoditolylmethane, and when *m*-tolylenediamine,  $\beta$ -naphthol and trioxymethylene are heated together, "aminomethylnaphthacridine" and its dihydro-(leuco) compound are formed in all cases (compare preceding

abstract). "Aminomethylnaphthacridine,"  $C_{10}H_6 \begin{array}{c} \text{C} \cdot \text{H} \\ \text{N} \end{array} \text{C}_6H_2Me \cdot NH_2$ , melts at  $244^\circ$  (corr.), is yellow, is a monoacid base, and forms coloured salts; of these, the *hydrochloride* and *platinichloride* were prepared. The *monocetyl* derivative melts at  $320-321^\circ$  (corr.), is almost colourless, and is readily hydrolysed by boiling dilute hydrochloric acid. "Aminomethyldihydronaphthacridine,"  $C_{18}H_{16}N_2$ , is almost colourless and melts at  $195-198^\circ$ . C. F. B.

Compounds of Iodoantipyrine with Mercuric Salts. By J. BOUGAULT (*J. Pharm.*, 1900, [vi], 11, 165-169).—*Iodoantipyrine mercuric chloride*,  $C_{11}H_{11}ON_2I, HgCl_2$ , forms beautiful, colourless crystals, melts and decomposes at  $168-169^\circ$ , and is stable in aqueous solution. Mercuric iodide does not combine directly with iodoantipyrine, but on adding iodine to an alcoholic solution of antipyrine containing mercuric iodide, the salt,  $2C_{11}H_{11}ON_2I, HgI_2$ , separates in bright yellow crystals. The compound,  $4C_{11}H_{11}ON_2I, HgI_2, HgI_2, 2HCl$ , prepared by mixing alcoholic solutions of the component salts, forms slightly yellow crystals, melts and decomposes at about  $140^\circ$ , and is rapidly

dissociated by water. The salt  $2C_{11}H_{11}ON_2I, HgI_2, HCl$  (this vol., i, 312) forms bright yellow crystals and melts and decomposes at  $130^\circ$ .

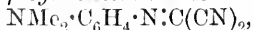
W. A. D.

**New Compound of Mercuric Chloride and Antipyrine.** By JULES VILLE and CHARLES ASTRE (*Compt. rend.*, 1900, 130, 837—840).—When a solution of mercuric chloride, containing also sodium chloride and hydrochloric acid, is added slowly to an aqueous solution of antipyrine, the compound  $(C_{11}H_{11}ON_2)_2, HHgCl_2$ , is obtained in rhomboidal lamellæ which melt at  $105$ — $106^\circ$ , and dissolve readily in chloroform. Its solutions give many of the ordinary reactions of mercuric compounds, but with sodium carbonate and sodium hydrogen carbonate there is no precipitate or turbidity, whilst potassium iodide yields a very slightly yellowish precipitate soluble in excess of the reagent to a yellowish solution. In the latter reactions, and also in its behaviour with stannous chloride and auric chloride, this compound differs from that described by Hirsch and by Schuyten (*Abstr.*, 1896, i, 575; and 1898, i, 452). It gives, however, the ordinary reactions of antipyrine.

C. H. B.

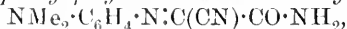
**Condensation of Aromatic Nitroso-compounds with Methylene Derivatives.** By FRANZ SACHS (*Ber.*, 1900, 33, 959—966. Compare *Abstr.*, 1899, i, 883).—4-Diethylaminophenyl- $\mu$ -cyanoazomethine-phenyl yields a crystalline *hydrochloride* when hydrogen chloride is passed into its benzene solution; in the perfectly dry state, this may be kept for months without undergoing decomposition; its chloroform solution is, however, decomposed when poured on to a dry filter paper. When the dye is heated with alcohol and hydroxylamine hydrochloride, it yields the oxime of benzoyl cyanide (*Abstr.*, 1888, 693). The *hydrochloride* of 4-diethylaminophenyl- $\mu$ -cyanoazomethine-4'-nitrophenyl is a lemon-yellow powder melting and decomposing at  $193^\circ$ .

4-Dimethylaminophenyl- $\mu$ -cyanoazomethinecarboxylonitrile,



is readily obtained when nitrosodimethylaniline and malonitrile are heated together in alcoholic solution, either with or without the addition of a few drops of sodium carbonate solution; it crystallises from alcohol in dark red crystals with a bronzy lustre, melts at  $167^\circ$ , and is insoluble in light petroleum; sulphuric acid hydrolyses it to dimethylphenylenediamine, carbon dioxide and hydrogen cyanide. The *diethyl* compound,  $NEt_2 \cdot C_6H_4 \cdot N : C(CN)_2$ , crystallises in brownish-violet needles or violet-red, glistening plates melting at  $114^\circ$ .

4-Dimethylaminophenyl- $\mu$ -cyanoazomethinecarboxylamide,

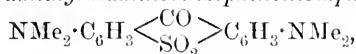


obtained from nitrosodimethylaniline and cyanoacetamide in the presence of alcohol and sodium carbonate solution, crystallises in rose-coloured, slender needles with a blue lustre, and melts at  $220$ — $221^\circ$ , the *diethyl* compound melts at  $165$ — $166^\circ$ , and is sparingly soluble in cold alcohol. A compound,  $SO_2 < \begin{smallmatrix} C_6H_3(NMe_2) \\ C_6H_3(NMe_2) \end{smallmatrix} > C : N \cdot C_6H_4 \cdot NMe_2$ ,

is obtained when an alcoholic solution of nitrosodimethylaniline and and tetramethyldiaminodiphenylmethanesulphone is warmed with a little sodium hydroxide solution; it is an orange-red powder, and is



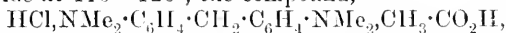
very sparingly soluble in the usual solvents. If the crude product is boiled, it yields *tetramethyldiaminobenzophenonesulphone*,



in the form of a yellowish-green precipitate which melts at  $317^\circ$  (corr.), sublimes at higher temperatures, and is extremely stable.

J. J. S.

**Action of Methyl Chloroacetate on Tertiary Bases.** By J. CENSI (*Chem. Centr.*, 1900, i, 594—595; from *Bull. Soc. ind. Mulhouse*, 70, 311—313).—Methyl chloroacetate,  $\text{CH}_3\text{Cl} \cdot \text{CO}_2\text{Me}$ , prepared by the action of chlorine on cold methyl acetate, boils at  $115^\circ$ . By condensing this compound (1 mol.) with dimethylaniline (2 mols.) in the presence of zinc chloride at  $110$ — $120^\circ$ , the compound,



is obtained. When methyl chloroacetate is poured into boiling water hydrochloric acid, acetic acid, and formaldehyde are formed.

E. W. W.

**Interaction of Hydrazine Hydrate with certain Lactones.** By JEAN WEDEL (*Ber.*, 1900, 33, 766—770).—*o*-Hydroxydiphenylacetic hydrazide,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , prepared by boiling *o*-hydroxydiphenylacetic lactone (Abstr., 1895, i, 419) dissolved in absolute alcohol with aqueous hydrazine hydrate, crystallises from absolute alcohol in microscopic, colourless, lustrous needles, and melts and decomposes at  $220^\circ$ ; it gives Bülow's reaction for phenylhydrazides, and dissolves in aqueous alkalis, being recovered unchanged by the action of carbon dioxide; this behaviour excludes the alternative formula,  $\text{CHPh} \begin{matrix} \text{O} \\ \text{C}_6\text{H}_4 \end{matrix} \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{NH}_2$ , for the substance. It unites at

the ordinary temperature with benzaldehyde, yielding the *benzylidene* derivative,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$ , which crystallises from alcohol in plates, and melts at  $171^\circ$ ; *o*-phthalaldehydic acid gives rise to the corresponding compound,



which dissolves in cold aqueous sodium carbonate, crystallises from alcohol in colourless plates, and decomposes at  $145^\circ$ .

*o*-Methylolbenzoic hydrazide,  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , prepared by gently warming aqueous hydrazine hydrate with an alcoholic solution of phthalide, crystallises from alcohol in long, slender needles, melts at  $128^\circ$ , and does not give Bülow's reaction; all attempts to

convert it into the dihydrophthalazone,  $\text{C}_6\text{H}_4 \begin{matrix} \text{CH}_2 \cdot \text{NH} \\ \text{CO} - \text{NH} \end{matrix}$ , by eliminating water by means of concentrated sulphuric acid, phosphorus pentachloride, or phosphorus oxychloride, yielded phthalide only. Attempts to prepare the same compound by the interaction of hydrazine hydrate with phthalide chloride,  $\text{CH}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ , were also fruitless. The *benzylidene* derivative,  $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}_2$ , obtained by the interaction of benzaldehyde with *o*-methylolbenzoic hydrazide, crystallises from alcohol in lustrous leaflets, and melts at  $145^\circ$ ; its *carboxylic acid*,

$C_{16}H_{14}O_4N_2$ , prepared similarly, using *o*-phthalaldehydic acid, forms needles, and melts at  $115^\circ$ .

No definite products could be isolated from the interaction of hydrazine hydrate with valerolactone or coumarin. Nitrous acid does not act on the hydrazides described, whilst acetic anhydride, instead of yielding acetyl derivatives, regenerates the original lactones.

W. A. D.

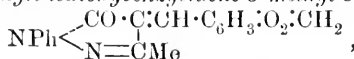
**Indogenides of the Pyrazole Series.** By JOSEF TAMBOR (*Ber.*, 1900, 33, 864—871. Compare Knorr, *Abstr.*, 1887, 601).— [With ERNST.] — 1-Phenyl-4-*o*-ethoxybenzylidene-3-methyl-5-pyrazolone,

$$NPh \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ | \\ \text{N} = \text{CMe} \end{array}$$
, prepared by heating 'technical pyrazolone' (1-phenyl-3-methyl-5-pyrazolone) with *o*-ethoxybenzaldehyde at  $135^\circ$  during 5—10 minutes, crystallises from alcohol in orange needles, and melts at  $142^\circ$ ; the solution in concentrated sulphuric acid is carmine. The corresponding *m*-ethoxy-compound crystallises in orange prisms, and melts at  $107^\circ$ ; the solution in sulphuric acid is brown, becoming yellow on dilution with water. The *p*-ethoxy-compound separates from dilute acetic acid in orange needles, and melts at  $130^\circ$ . The *p*-methoxy-compound, prepared from pyrazolone and anisaldehyde, crystallises from alcohol, and melts at  $128.5^\circ$ ; the solution in concentrated sulphuric acid is yellow. The *p*-hydroxy-compound crystallises in orange needles and melts at  $226^\circ$ , forming a greenish-yellow solution in concentrated sulphuric acid; the *acetyl* derivative melts at  $137^\circ$ .

[With LICIŃSKI.] — 1-Phenyl-4-*p*-hydroxy-*m*-methoxybenzylidene-3-methyl-5-pyrazolone, 
$$NPh \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{OH} \\ | \\ \text{N} = \text{CMe} \end{array}$$
, prepared from pyrazolone and vanillin, crystallises from ether in lustrous, red prisms, and melts at  $169^\circ$ ; the *acetyl* derivative melts at  $143$ — $144^\circ$ . The *mp*-dimethoxy-compound forms long, lustrous needles, and melts at  $160^\circ$ , dissolving in sulphuric acid to an orange liquid.

4-*p*-Hydroxy-*m*-methoxybenzylidene-bis-1-phenyl-3-methyl-5-pyrazolone,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH}(\text{C}_{10}\text{H}_9\text{ON}_2)_2$ , produced on heating vanillin with 2 mols. of pyrazolone at  $160^\circ$  for 10 minutes, crystallises from alcohol in yellow needles, and melts at  $209^\circ$ ; the solution in concentrated sulphuric acid is orange.

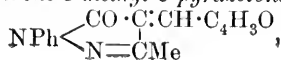
1-Phenyl-*mp*-methylenedioxybenzylidene-3-methyl-5-pyrazolone,



prepared from pyrazolone and piperonaldehyde, crystallises from alcohol in deep red, lustrous needles, and melts at  $166$ — $167^\circ$ .

4-*mp*-Methylenedioxybenzylidene-bis-1-phenyl-3-methyl-5-pyrazolone,  $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{C}_{10}\text{H}_9\text{ON}_2)_2$ , obtained on heating piperonaldehyde with 2 mols. of pyrazolone, crystallises in small, white needles, which melt and evolve gas at  $143^\circ$ ; the solution in concentrated sulphuric acid is reddish-yellow.

1-Phenyl-4-furfurylidene-3-methyl-5-pyrazolone,



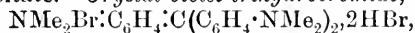
prepared from furfuraldehyde and pyrazolone, crystallises from alcohol in violet needles, and melts at 111—112°; the solution in concentrated sulphuric acid is brownish-black.

4-Furfurylidene-bis-1-phenyl-3-methyl-5-pyrazolone,  
 $C_4H_3O \cdot CH(C_{10}H_9ON_2)_2$ ,

produced on heating furfuraldehyde with 2 mols. of pyrazolone, crystallises from alcohol in pale brown prisms, and melts at 172—173°; when treated with concentrated sulphuric acid, the crystals become blue, a green solution being formed. M. O. F.

**Tertiary Aromatic Amines. III.** By CARL HAEUSSERMANN (*Ber.*, 1900, 33, 939—941. Compare *Abstr.*, 1899, i, 204 and 684).—*Nitrotetraphenyl-o-phenylenediamine*,  $C_{30}H_{23}O_2N_3$ , prepared by the action of nitrous acid on tetraphenyl-o-phenylenediamine, crystallises from glacial acetic acid in brownish-yellow needles and melts at 186—187°. *m*-Dichlorobenzene, when treated with potassium diphenylamine, gives the same condensation product as *o*-dichlorobenzene, owing to isomeric change, and the nitro-derivatives are also identical;  $\beta$ -tetraphenyl-phenylenediamine, however, appears to be an entirely different compound, in spite of the proximity of the melting points. T. M. L.

**Salts and Bases of Triphenylmethane Dyes.** By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 752—760. Compare Hantzsch and Osswald, this vol., i, 256).—By leading dry hydrogen bromide into a solution of the leuco-base in ether-acetone at  $-15^\circ$ , *crystal-violet-leucohydroxide trihydrobromide*,  $OH \cdot C(C_6H_4 \cdot NMe_2)_3 \cdot 3HBr$ , separates as a white, flocculent precipitate. *Crystal-violet trihydrobromide*,



is precipitated as a reddish powder on passing hydrogen bromide into a warm solution of the colour base; it dissolves in water with a deep violet colour even at  $0^\circ$ , owing to decomposition into the monoacid salt and hydrogen bromide.

The salts of the colour-base have a much higher conductivity than the carbinol salt; thus crystal-violet trihydrochloride gave  $\mu_{256}$  774 at  $25^\circ$ , and crystal-violet carbinol trihydrobromide gave  $\mu_{256}$  471; the carbinol trihydrobromide gradually passes in solution into the trihydrobromide of the colour-base, the conductivity increasing in one experiment from  $\mu_{261}$  452 to 792. The carbinol trihydrobromide resembles the aniline salts in that it is partially hydrolysed in solution, but the colour-trihydrobromide decomposes in solution into 2 mols. of hydrogen bromide, and the monohydrobromide, which is ionised, but not hydrolysed, since the colour-base is comparable with potassium hydroxide rather than with aniline.

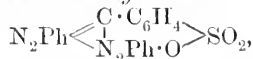
On adding sodium hydroxide to a dilute solution of magenta, or 'new-magenta,' the ammonium colour-base is first formed (rosanilinium hydroxide), but with an excess of alkali a red, flocculent precipitate separates which dissolves readily in ether, benzene, or acetone to a reddish-yellow solution, and is readily precipitated by carbon dioxide as a dark red carbonate (Homolka, Nietzki's "*Chemie der organischen Farbstoffe*," p. 119); this is regarded as an imide-base,  $NH : C_6H_4 : C(C_6H_4 \cdot NH_2)_2$ , the anhydride of the rosanilinium hydroxide,  $OH \cdot NH_2 : C_6H_4 : C(C_6H_4 \cdot NH_2)_2$ , into which it rapidly passes in solution, or in the solid state, or

when dried, or when left in contact with the solution from which it is precipitated; when changed in this way, the colour disappears and the base is no longer precipitated by carbon dioxide. The imide-base could not be analysed, but no such bases are formed from the completely alkylated colour-salts, thus confirming the view that they are formed by loss of 1 mol. of water; this view is also confirmed by their solubility in ether, since the mixture of 1 mol. magenta and 1 mol. sodium hydroxide cannot be extracted with ether. T. M. L.

**Colouring Matters of the Formazyl Group.** By FRITZ FICHTER and EMANUEL SCHIESS (*Ber.*, 1900, 33, 747—752).—*Sodium formazylbenzene-II-p-sulphonate*,  $\text{N}_2\text{Ph}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ , prepared by the action of diazobenzene on sodium phenylbenzylidenehydrazone-*p*-sulphonate, crystallises from alcohol in minute, dark red needles, decomposes at about  $135^\circ$ , and dyes silk and wool a dark red colour; when warmed with sulphuric and acetic acids, it gives 3-phenylphenotriazine,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{CPh} \end{smallmatrix}$ , and aniline, but no sulphanilic acid; with zinc dust and sulphuric acid, it gives phenylhydrazine and *s*-benzoylphenylhydrazine-*p*-sulphonic acid,  $\text{COPh}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , which crystallises from water in thin, colourless flakes.

*Sodium formazylbenzene-III-p-sulphonate*,  $\text{NHPH}\cdot\text{N}\cdot\text{CPh}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ , prepared by the action of diazobenzene-*p*-sulphonic acid on phenylbenzylidenehydrazone, crystallises from alcohol in minute, red needles, decomposes at about  $165^\circ$ , and dyes a somewhat brighter colour than the preceding isomeride; like its isomeride, it gives with sulphuric acid phenylphenotriazine in place of the expected sulphonic acid, and with zinc dust and sulphuric acid gives *s*-benzoylphenylhydrazine-*p*-sulphonic acid.

*Sodium formazylbenzene-I-m-sulphonate*,  $\text{N}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na})\cdot\text{N}\cdot\text{NHPH}$ , prepared by the action of diazobenzene on the condensation product of sodium benzaldehyde-*m*-sulphonate and phenylhydrazine, crystallises from alcohol in red needles, and is much more soluble than the preceding isomerides. On oxidation with nitrous acid, it gives the inner anhydride of triphenyltetrazoliumhydroxide-I-m-sulphonic acid,



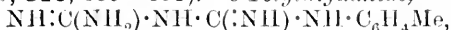
which crystallises from dilute hydrochloric acid in small, four-sided tablets, does not melt at  $250^\circ$ , and is not attacked by acids, but is decomposed by alkalis with formation of a red coloration. The isomerides are still less soluble and are less well characterised.

*II-Phenyl-III- $\alpha$ -naphthylformazylbenzene*,  $\text{NHPH}\cdot\text{N}\cdot\text{CPh}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7$ , crystallises from benzene in dark violet needles with a green metallic lustre, and melts at  $173^\circ$ ; with sulphuric acid, it gives aniline and phenyl-naphthotriazine,  $\text{C}_{10}\text{H}_6\begin{smallmatrix} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{CPh} \end{smallmatrix}$ , which crystallises from alcohol in yellowish-green needles and melts at  $145^\circ$ .

*III-Phenyl-II- $\alpha$ -naphthylformazylbenzene*,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{N}\cdot\text{CPh}\cdot\text{N}_2\text{Ph}$ ,

crystallises from benzene or from a mixture of alcohol and chloroform in deep violet needles and melts at 144—145°; it gives the same triazine as the preceding isomeride. T. M. L.

**Tolyldiguanides and Benzyldiguanide.** By ERNST BEUTEL (*Annalen*, 1900, 310, 335—351).—*o*-Tolyldiguanide,



crystallises from water in nacreous plates containing  $\frac{1}{2}\text{H}_2\text{O}$ , and melts at 144°; boiling alkalis liberate *o*-toluidine, and the aqueous solution yields precipitates with salts of copper, nickel, cobalt, or silver. The *hydrochloride*, prepared by heating *o*-toluidine hydrochloride with dicyanodiamide in molecular proportion, crystallises from water in large, colourless prisms containing  $\frac{1}{2}\text{H}_2\text{O}$ , which is removed by exposure to dried air; the anhydrous substance melts at 229°. The *platinichloride* crystallises from dilute hydrochloric acid in orange-red, rhombic plates, and melts at 199°.

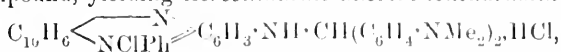
*m*-Tolyldiguanide,  $\text{C}_9\text{H}_{13}\text{N}_5$ , crystallises in nacreous scales containing  $3\text{H}_2\text{O}$ , and melts at 76°; the *hydrochloride*, which contains  $\frac{1}{2}\text{H}_2\text{O}$ , crystallises in the monosymmetric system, and melts at 211°.

*p*-Tolyldiguanide,  $\text{C}_9\text{H}_{13}\text{N}_5$ , crystallises in colourless leaflets and melts at 152°; the *hydrochloride* contains  $\frac{1}{2}\text{H}_2\text{O}$  and melts at 235°; the *sulphate* is anhydrous, and the *chromate*, which contains  $2\frac{1}{2}\text{H}_2\text{O}$ , decomposes at 166°.

*Benzyldiguanide*,  $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , absorbs carbon dioxide so readily that an examination of the substance is a matter of some difficulty; the *hydrochloride*, prepared by heating benzylamine hydrochloride with dicyanodiamide, crystallises in colourless, lustrous plates, and melts at 197°, decomposing above 260°.

A summary of the general properties of these substances and their solubility relationships concludes the paper. M. O. F.

**Action of Tetramethyldiaminobenzhydrol on Rosinduline and on Isorosinduline.** By RICHARD MÜHLAU and W. SCHAPO-SCHNIKOFF (*Ber.*, 1900, 33, 799—803).—Rosinduline chloride does not react with tetramethyldiaminobenzhydrol, whereas Nietzki-Otto's isorosinduline chloride readily reacts with an alcoholic solution of the same compound, yielding *isorosinduline chloride-leucauramine*,



which crystallises with  $5\text{H}_2\text{O}$ . It dissolves readily in alcohol, and moderately in water, to reddish-violet solutions which do not exhibit fluorescence; acid liquids readily hydrolyse it, even in the cold, as also do neutral salts such as sodium chloride or nitrate. The *base* crystallises from benzene or ether in violet, acicular prisms. The *chromate*, *picrate*, *tannate*, and double salts with zinc, mercury, gold, or platinum are all insoluble in water. The *platinichloride*,  $\text{C}_{39}\text{H}_{37}\text{N}_5\text{PtCl}_6$ , forms a reddish-violet, crystalline precipitate. J. J. S.

**Dynamical Researches on the Formation of Azo-Dyes.** IV. By HEINRICH GOLDSCHMIDT and GUSTAV KEPPELER (*Ber.*, 1900, 33, 893—905. Compare Abstr., 1897, i, 278; 1898, ii, 20; 1899, ii, 276).—The reaction of sodium benzenediazotate with sodium  $\beta$  naphthoxide

and *m*-tolylxide has been investigated, and the results are found to confirm the conclusion arrived at already, namely, that the actual "coupling" takes place between the diazobenzene hydroxide and the phenol, which exist in the solution owing to the hydrolysis of the respective salts. Further experiments with sodium *syn*-diazobenzenesulphonate and *m*-tolylxide confirm the previous results, and show that the presence of a considerable quantity of potassium chloride has little influence on the velocity of the reaction. Experiments with thymol and sodium benzenediazotate or *syn*-diazobenzenesulphonate did not give satisfactory results.

Experiments were also made with an isodiazo-compound: sodium *p*-nitrobenzeneisodiazoate ("nitrosamine-red") was allowed to react with sodium  $\beta$ -naphthoxide at 20; in the estimation of the unchanged isodiazo-compound, it was found necessary to add cuprous chloride solution, as mere boiling with dilute acid did not suffice to expel all the nitrogen. In this case, as in the others, it was found that the times in which equal fractions are transformed are proportional to the concentrations, and that excess of alkali hydroxide retards the reaction. Curiously enough, however, the numerical results are rather in harmony with the supposition that of one of the substances it is the hydrolysed part that reacts, whilst the other substance reacts as if its concentration were constant.

C. F. B.

Abel's Dibenzeneazo- $\beta$ -dinaphtholmethane and Dinitroso- $\beta$ -dinaphtholmethane. By RICHARD MOHLAU and ERICH STROHBACH (*Ber.*, 1900, 33, 804—807).—These two compounds described by Abel (*Abstr.*, 1893, i, 172) are shown to be respectively benzeneazo- $\beta$ -naphthol and  $\alpha$ -nitroso- $\beta$ -naphthol. Slight modifications in the preparation of  $\beta$ -dinaphtholmethane are recommended.

J. J. S.

Phenylcarbamic Ester of Epinephrine. By JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xvii—xviii).—The formation of a substance which is shown to be the sulphate of epinephrine phenylcarbamate,  $C_{17}H_{13}O_2N(CO_2 \cdot NHPh)_2 \cdot H_2SO_4$ , is believed to demonstrate that epinephrine is a chemical individual. Although two of the hydroxyl groups have entered into combination with phenylcarbamide, physiological activity is retained.

W. D. H.

Action of Triethylphosphine on  $\omega\omega_1$ -Dibromo-*o*-xylene. By ALFRED PARTHEIL and A. GRONOVER (*Ber.*, 1900, 33, 606—607).— $\omega\omega_1$ -Dibromo-*o*-xylene reacts with triethylphosphine dissolved in chloroform to form *o*-xyllyleneditriethylphosphonium bromide,  $C_6H_4(CH_2 \cdot PET_3Br)_2$ , a neutral substance forming colourless crystals which melt at 250—250.5°. The corresponding base is strongly alkaline and very unstable; the hydriodide,  $C_6H_4(CH_2 \cdot PET_3I)_2 \cdot 2HI$ , melts at 247°. The aurichloride,  $C_6H_4(CH_2 \cdot PET_3 \cdot AuCl_4)_2$ , crystallises in yellow needles melting at 163°, and the platinichloride,  $C_6H_4(CH_2 \cdot PET_3)_2PtCl_6$ , is an amorphous powder which melts at 235—236°.

R. H. P.

## Organic Chemistry.

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**Relation Between Boiling Point and Melting Point in the Hydrocarbons.** By THOMAS BAYLEY (*Chem. News*, 1900, 81, 1—3).—The ratio (boiling point under 760 mm. pressure)/(melting point) in the paraffin series varies from 1.25 for  $\text{CH}_4$  to 2.0 for  $\text{C}_{19}\text{H}_{40}$ . Above  $\text{C}_{19}$ , the boiling point is taken at 15 mm. pressure and the ratio varies between 1.53 and 1.73 for the higher members of the series; altogether, the boiling point rises relatively more than the melting point. The values of the ratio are deduced for the ethylene and acetylene series as well as for a number of closed chain hydrocarbons, but no general law is laid down which governs these values. J. C. P.

**Action of Anhydrous Aluminium Chloride on Acetylene.** By E. BAUD (*Compt. rend.*, 1900, 130, 1319—1322. Compare Alexander, Abstr., 1899, i, 843).—Dry acetylene is completely absorbed by anhydrous aluminium chloride even in the cold, and at  $70^\circ$  the absorption is complete in a few minutes. When the gas is passed over the chloride, heated at  $70$ — $130^\circ$ , 4 parts of the former are absorbed and a black sublimate is obtained the composition of which corresponds with  $7(\text{C}_{10}\text{H}_{15.6}), 2\text{Al}_2\text{Cl}_6$ ; this substance is insoluble and readily oxidisable; it is decomposed by moisture, yielding a light yellow powder which even after prolonged washing still contains both aluminium and chlorine; when distilled with quick lime, it gives off a mixture of hydrocarbons ( $\text{C}_{10}\text{H}_{14}$ ,  $\text{C}_{10}\text{H}_{16}$ , and  $\text{C}_{10}\text{H}_{18}$ ) boiling from  $150^\circ$  to  $306^\circ$ . The greater portion of the aluminium chloride and acetylene, however, combine to form a non-volatile, black substance; this product contains less hydrogen than the sublimate, having the empirical formula  $7(\text{C}_{20}\text{H}_{15}), \text{Al}_2\text{Cl}_6$ ; it is very insoluble in the ordinary solvents, reduces permanganate in the cold, and on distillation with quick lime yields a small amount of the hydrocarbons,  $\text{C}_{15}\text{H}_{20}$ , boiling at  $150$ — $350^\circ$ ; the less volatile portions are almost solid and contain anthracene.

G. T. M.

**Bromination by means of Aluminium Bromide.** By CHARLES POURET (*Compt. rend.*, 1900, 130, 1191—1192).—The following bromides were obtained by the action of aluminium bromide on the corresponding chlorides, the bromination being effected either in a flask or in a sealed tube; bromoform, methyl bromide, methylene bromide, ethyl bromide, ethylene dibromide, ethylidene dibromide, acetylene tetrabromide, and pentabromoethane. H. R. LE S.

**Reactivity of the Hydrogen Atoms in Disulphones, Trisulphones, and Tetrasulphones.** By ARTHUR KÖRZ (*Ber.*, 1900, 33, 1120—1127).—The dimethyl and diethyl derivatives,  $\text{C}_2\text{H}_6:(\text{SO}_2)_2:\text{CMe}_2$  and  $\text{C}_2\text{H}_6:(\text{SO}_2)_2:\text{CEt}_2$ , of tetramethylene-1:3-disulphone, can be obtained by the direct alkylation of the latter as well as by the method of Autenrieth and Wolff (Abstr., 1899, i, 581). Disulphones containing the group  $\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot$  were found to be indifferent to nitrous acid and to diazobenzene hydrate, although the formation of

isonitroso-compounds and hydrazones was looked for. Experiments with acetaldehyde, benzaldehyde, nitrobenzaldehyde, chloral, &c., show that, in general, the  $\cdot\text{CH}$  radicle of the disulphones,  $\text{CHR}:(\text{SO}_2\text{R}')_2$ , is as indifferent towards aldehydes as the  $\cdot\text{CH}$  radicle in the compounds  $\text{CHR}(\text{CO}_2\text{H})_2$ ,  $\text{CO}_2\text{H}\cdot\text{CHR}\cdot\text{CO}\cdot\text{R}$ ,  $\text{CHPhR}\cdot\text{CN}$ ,  $\cdot\text{CO}\cdot\text{CHR}\cdot\text{CO}\cdot$ ; similarly, the methylene group in the disulphones,  $\text{CH}_2(\text{SO}_2\text{R}')_2$ , is less reactive than the methylene groups present in the compounds of which the foregoing substances are R-substitution derivatives. The behaviour of formaldehyde with the disulphones,  $\text{CH}_2(\text{SO}_2\text{R})_2$ , however, is exceptional, giving rise to *tetrasulphones* of the type  $\text{CH}_2[\text{CH}(\text{SO}_2\text{R})_2]_2$ ; this behaviour is analogous to the interaction of formaldehyde with ethyl malonate (Knoevenagel, *Abstr.*, 1894, i, 570) and with ethyl acetoacetate (*Ber.*, 1893, 26, 1087).

*Tetraethyltetrasulphone*,  $\text{CH}_2[\text{CH}(\text{SO}_2\text{Et})_2]_2$ , obtained from methylenediethylsulphone and formaldehyde, in presence of a secondary base such as diethylamine as condensing agent, forms colourless crystals; the analogous *tetrapropyl-* and *tetraisopropyl-*derivatives melt at  $156-157^\circ$  and  $129.5^\circ$  respectively; *di-trimethylenetetrasulphone*,  $\text{CH}_2\left(\text{CH}\begin{smallmatrix} \text{SO}_2\cdot\text{CH}_2 \\ \text{SO}_2\cdot\text{CH}_2 \end{smallmatrix}\text{CH}_2\right)_2$ , melts above  $300^\circ$ .

The behaviour of trimethylenedisulphone with formaldehyde is exceptional; in presence of diethylamine, hydroxyethylsulphonemethylenesulphonic acid,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{H}$ , is formed, but without the condensing agent, heating on the water-bath for 6 hours produces a crystalline substance,  $\text{CH}_2\begin{smallmatrix} \text{SO}_2\cdot\text{CH}_2 \\ \text{SO}_2\cdot\text{CH}_2 \end{smallmatrix}, 2\text{CH}_2\text{O}$ , which melts and decomposes at  $238^\circ$ .

The tetrasulphones are, as a class, sparingly soluble in water, form well-defined crystals, and are indifferent towards cold concentrated sulphuric and nitric acids; they combine with bromine, yielding dibromo-derivatives of the type  $\text{CH}_2[\text{CBr}(\text{SO}_2\text{R})_2]_2$ , which are decomposed by dilute alkalis, regenerating the original tetrasulphone; *dibromotetraethyltetrasulphone* melts at  $176^\circ$ . Tetrasulphones are not changed when warmed with 15 per cent. aqueous sodium hydroxide, but if heated for several hours at  $100^\circ$ , are resolved into formaldehyde and the disulphone  $\text{CH}_2(\text{SO}_2\text{R})_2$ . Methyl iodide, in presence of sodium hydroxide, does not yield a methyl derivative of the tetrasulphone, but gives rise to the dimethyl derivative,  $\text{CMe}_2(\text{SO}_2\text{R})_2$ , of the disulphone initially formed by the action of the alkali. Thus, from tetraethyltetrasulphone, under these conditions, sulphonol is obtained.

In discussing the influence of two sulphone groups on the reactivity of the methylene group to which they are attached, it is shown that the disulphones  $\text{CH}_2(\text{SO}_2\text{Et})_2$  and  $\text{CHMe}(\text{SO}_2\text{Et})_2$  are practically non-conducting in solution, and therefore, like ethyl malonate, and unlike ethyl acetoacetate, cannot be regarded as weak acids; diethylsulphone-phenylsulphonemethane,  $\text{CH}(\text{SO}_2\text{Et}_2)\cdot\text{SO}_2\text{Ph}$ , on the other hand, from its conductivity, appears to be a strong monobasic acid. W. A. D.

**Action of Chloral on the Chloroacetic Acids.** By EMILIO GABUTTI (*Gazzetta*, 1900, 30, 253-257).—Chloral reacts with the chloroacetic acids, yielding the corresponding chloroacetates.



*Chloral chloroacetate*,  $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{CH}_2\text{Cl})_2$ , which is obtained in about a 50 per cent. yield, is a colourless oil with a pungent, aromatic odour, and is very soluble in ether. The *dichloroacetate*,  $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{CHCl}_2)_2$ , obtained in small yield only, is an oil having an indefinite, aromatic odour; it boils at  $230^\circ$  and dissolves in ether. The *trichloroacetate*,  $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{CCl}_3)_2$ , is formed in small quantity as a colourless oil with a pleasing aromatic odour; it boils at  $240$ — $242^\circ$ , and is soluble in ether.

T. H. P.

**Organic Peroxides. IV.** By LUDWIG VANINO and EMIL UHLFELDER (*Ber.*, 1900, 33, 1043—1051. Compare Abstr., 1894, i, 416; 1896, i, 597; 1897, i, 621).—In the preparation of *chloroacetyl peroxide* by von Pechmann and Vanino's method (Abstr., 1894, i, 416), it is advisable to employ sodium acetate instead of sodium hydroxide solution, and to see that the mixture is kept well cooled and thoroughly shaken. It crystallises in small needles, melts at  $36^\circ$ , decomposes at  $85^\circ$ , and dissolves readily in most solvents, with the exception of light petroleum. It explodes under pressure or when struck, but when heated on platinum merely burns; it also explodes when mixed with aluminium, lead peroxide, sulphur, or potassium chlorate. *Trichloroacetyl peroxide* decomposed so readily that it could not be examined in detail.

*m*-Nitrobenzoyl peroxide (Brodie, *Annalen, Supp.*, 3, 209; Vanino, Abstr., 1897, i, 621) may be obtained by adding benzoyl peroxide to a well cooled mixture of concentrated nitric and sulphuric acids, or by the action of alkaline hydrogen peroxide on an acetone solution of *m*-nitrobenzoyl chloride.

The oxidation of *p*-nitrobenzoyl chloride to the peroxide only takes place when pyridine is employed instead of sodium hydroxide; the *peroxide* forms yellow crystals, melts at  $151^\circ$ , and readily decomposes.

*o*-Bromobenzoyl peroxide, obtained by the action of hydrogen peroxide and pyridine on the chloride, crystallises in colourless needles, detonates at  $114^\circ$ , and is readily soluble in most organic solvents; the *m*-bromo-compound melts at  $132^\circ$ , and the *p*-bromo-derivative detonates at  $152^\circ$ .

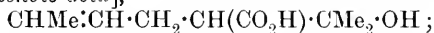
It has not been found possible to isolate *o*-iodobenzoyl peroxide in a state of purity; the crude product melts between  $68^\circ$  and  $90^\circ$ . When this crude product is dissolved in boiling acetic acid and the solution then treated with light petroleum, an acid melting at  $228^\circ$ , and isomeric with Meyer and Wachter's iodosobenzoic acid, is obtained; from hot water, in which it is much more readily soluble than Meyer and Wachter's acid, it crystallises in small needles, and dissolves in alkalis yielding colourless solutions; it does not yield an acetyl derivative when treated with acetic anhydride. The authors suggest that their acid has the constitution  $\text{OI} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , and Meyer's acid the constitution  $\text{C}_6\text{H}_4 \cdot \text{I}(\text{OH}) \text{CO}_2\text{H}$  (compare Abstr., 1892, i, 1460).

J. J. S.

**Cineolic Acid.** By HANS RUPE (*Ber.*, 1900, 33, 1129—1140).—Cineolic acid, when heated with water at  $160^\circ$  for 3 hours, yields a mixture of two isomeric acids,  $\text{C}_9\text{H}_{16}\text{O}_3$ ; the first of these, *cineic acid*, is stable towards aqueous potassium permanganate, does not interact with bromine, phenylhydrazine, hydroxylamine, or semicarbazide, and

thus appears to have the structure  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CMe}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$ .

The second acid, which appears to be formed by the action of water at  $160^\circ$  on cinenic acid, since a yield of 50 per cent. can be obtained in this way from the latter, is a *methoethylol-5-hexene-2-acid-6* [ *$\alpha$ -hydroxyisopropyl- $\Delta^7$ -hexenoic acid*],



this view of its structure is supported by its decolorising aqueous potassium permanganate, by its combining directly with 1 mol. of bromine, and by its losing water, when heated, in the manner characteristic of  $\beta$ -hydroxy-acids, yielding *methoethene-5-hexene-2-acid-6* [ *$\alpha$ -isopropylidene- $\Delta^7$ -hexenoic acid*],  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{CMe}_2$ .

*Cinenic acid* crystallises from light petroleum in beautiful, transparent crystals, melts at  $83-84^\circ$ , and boils at  $127.5-129.5^\circ$  under 14 mm. and at  $245-247^\circ$  under atmospheric pressure; whilst *cineolic acid* has  $\lambda_{1024} - \lambda_{32} = 27.02$  at  $18^\circ$ , *cinenic acid* has  $\lambda_{1024} - \lambda_{32} = 70.03$ . The *silver* salt forms slender white needles, and the *calcium* salt (with  $2\text{H}_2\text{O}$ ) a microcrystalline mass; the *methyl* ester is a colourless liquid, which boils at  $86-89^\circ$  under 14 mm. pressure, and has a camphor-like odour; the *ethyl* ester boils at  $111-113^\circ$  under 17 mm. pressure. When *cinenic acid* is esterified by passing hydrogen chloride into its alcoholic solution, fission of the ring occurs, and *ethyl  $\delta$ -chloro- $\alpha$ -methoethylolhexoate*,



is apparently formed; the ester isolated, however, which boiled at  $131-136^\circ$ , was by no means pure.

$\alpha$ -Hydroxyisopropyl- $\Delta^7$ -hexenoic acid crystallises from water in small, white, nacreous leaflets, from light petroleum in matted, silky needles, melts at  $59-60^\circ$ , and boils at  $152-153^\circ$  under 10 mm. pressure; the *silver* salt is amorphous, and the *magnesium* salt (with  $2\text{H}_2\text{O}$ ) microcrystalline.  $\alpha$ -iso-Propylidene- $\Delta^7$ -hexenoic acid, obtained by distilling the foregoing acid under atmospheric pressure, boils at  $136-138^\circ$  under 11 mm. pressure, has a sp. gr. 0.9816 at  $17^\circ$ ,  $\mu_D = 7.48$ , a molecular refraction 44.57, and is transparent and colourless; in the air, it gradually becomes yellow and finally resinifies; the *silver* salt is amorphous and unstable, and the *calcium* salt (with  $1\text{H}_2\text{O}$ ) forms sheaf-like aggregates of microscopic needles.

*Ethyl hydrogen cineolate*,  $\text{CO}_2\text{H} \cdot \text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CO}_2\text{Et}$ , crystallises from dilute alcohol, or better from petroleum of high boiling point, in slender needles, and melts at  $99-100^\circ$ . When *cineolic acid* is heated for several hours at  $160-165^\circ$  with 10 per cent. aqueous sulphuric acid, there is formed a considerable amount of the acid  $\text{C}_9\text{H}_{16}\text{O}_3$ , obtained by Wallach and Gildemeister in very minute quantity by the dry distillation of *cineolic acid*. The foregoing results accord well with Wallach's formula,  $\text{CO}_2\text{H} \cdot \text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CMe}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$ , for *cineolic acid*.

W. A. D.

Preparation of Ethyl  $\beta$ -Alkoxy- $\alpha$ -cyanocrotonates Isomeric with Ethyl Cyanoalkylacetoacetates. By ALBIN HALLER (*Compt. rend.*, 1900, 130, 1221-1225).—Ethyl  $\beta$ -ethoxy- $\alpha$ -cyanocroto-

*nate*, the isomeride of ethyl cyanoethylacetoacetate, is prepared by treating the silver derivative of ethyl cyanoacetoacetate with a slight excess of ethyl iodide on the water-bath; it crystallises from ether in colourless needles melting at  $76^{\circ}$ , and dissolves in the ordinary organic solvents, but not in water or aqueous solutions of alkali hydroxides. When treated with alcoholic potash, it is hydrolysed into ethyl alcohol and the potassium derivative of ethyl cyanoacetoacetate; with hydrochloric acid, it undergoes a similar decomposition, yielding ethyl chloride and ethyl cyanoacetoacetate.

*Ethyl  $\beta$ -amino- $\alpha$ -cyanocrotonate*, obtained by treating the preceding compound with aqueous ammonia, separates from alcohol in prismatic crystals and melts at  $188^{\circ}$ ; it is identical with the compound obtained in small quantities by the action of ammonia on ethyl cyanoacetoacetate itself.

*Ethyl  $\beta$ -methoxy- $\alpha$ -cyanocrotonate*, produced by employing methyl iodide in the above condensation, crystallises in needles melting at  $134^{\circ}$ .

The corresponding  *$\beta$ -propyloxy-*,  *$\beta$ -isobutyloxy-*, and  *$\beta$ -benzyloxy-*esters melt at  $85-86^{\circ}$ ,  $94$ , and  $113^{\circ}$  respectively.

The formation of substituted  *$\beta$ -alkoxycrotonates* from ethyl cyanoacetoacetate raises the question as to whether this substance is not in reality a  *$\beta$ -hydroxy- $\alpha$ -cyanocrotonate*. On the other hand, the tautomeric change may occur when the ester is converted into its metallic derivative.

G. T. M.

**Ethyl Acetoacetate.** II. By HEINRICH GOLDSCHMIDT and LAZAR OSLAN (*Ber.*, 1900, 33, 1140—1152. Compare this vol., i, 132).—By using a purer preparation of ethyl acetoacetate, the value of the affinity constant at  $25^{\circ}$  has been reduced from  $k = 0.63 \times 10^{-7}$  to  $k = 0.4 \times 10^{-8}$ , but is probably still too high. By determining the velocity constant of the hydrolysis of the ester by weak bases, the value  $k = 2 \times 10^{-11}$  has been obtained. The hydrolytic constant of ethyl sodioacetoacetate is then calculated to be  $0.65 \times 10^{-5}$ .

The hydrolysis of ethyl dimethylacetoacetate by sodium hydroxide is more rapid than that of ethyl acetoacetate, and proceeds in a normal way as a reaction of the second order, the velocity constant being  $k = 2.85$  at  $25^{\circ}$ .

T. M. L.

**Acetylation of Ethyl Acetoacetate.** By LUDWIG CLAISEN and E. HAASE (*Ber.*, 1900, 33, 1242—1246. Compare Abstr., 1896, i, 557).—Pure ethyl O-acetylacetoacetate,  $\text{CH}_3 \cdot \text{C}(\text{OAc}) : \text{CH} \cdot \text{CO}_2\text{Et}$ , can readily be prepared by the action of acetyl chloride (freed from hydrogen chloride by distilling over dimethylaniline) on a mixture of ethyl acetoacetate and pure dry pyridine. It boils at  $104-105^{\circ}$  under 10 mm. and at  $214-216^{\circ}$  with slight decomposition, under atmospheric pressure, is insoluble in alkalis, and not readily attacked by them.

*Ethyl O-acetyldiacetoacetate*,  $\text{CH}_3 \cdot \text{C}(\text{OAc}) : \text{CAc} \cdot \text{CO}_2\text{Et}$ , prepared in a similar way, boils at  $142-144^{\circ}$  under 10 mm., but decomposes completely when distilled under atmospheric pressure; it is a pale yellow oil and is decomposed by water and alkalis as readily as acetic anhydride. The isomeric ethyl triacetoacetate,  $\text{CAc} : \text{CO}_2\text{Et}$ , is not known, and is probably too unstable to exist.

T. M. L.

**Action of Ethyl Chloroacetate on Sodioacetylacetone.** By F. MARCH (*Compt. rend.*, 1900, 130, 1192—1194).—*Ethyl  $\beta\beta$ -diacetylpropionate*,  $\text{CH}_3\text{Ac}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained by heating molecular proportions of ethyl chloroacetate and sodioacetylacetone at  $150^\circ$  for 8 hours, is a yellow liquid boiling at  $146\text{--}147^\circ$  under 24 mm. pressure, and is insoluble in water, but readily dissolves in alcohol and ether. Its alcoholic solution gives a greyish precipitate with cupric acetate. Its *phenylhydrazone* readily loses 1 mol. of water, giving *ethyl dimethylphenylpyrazoleacetate*,  $\text{NPh} \begin{array}{l} \text{N}=\text{CMe} \\ \text{CMe}:\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \end{array}$

*Methyl  $\beta\beta$ -diacetylpropionate*, obtained in a similar way, is a nearly colourless liquid boiling at  $130\text{--}132^\circ$  under 24 mm. pressure. It is readily soluble in ethyl alcohol, methyl alcohol, and ether, but is insoluble in water. H. R. LE S.

**Conversion of Dimethylmaleic Anhydride into Dimethylfumaric Acid.** By ETTORE MOLINARI (*Ber.*, 1900, 33, 1408—1419).—The normal methyl ester of dimethylmaleic acid distils at  $219^\circ$ , has a sp. gr. 1.1216 at  $0^\circ/0^\circ$ , and dissolves readily in most organic solvents. The ethyl ester distils at  $237^\circ$ . When either ester is heated for 24 hours at  $100\text{--}106^\circ$  with alcohol saturated at  $0^\circ$  with ammonia, a crystalline product, *aminodimethylsuccinimide*,  $\text{NH}_2\cdot\text{CMe} \begin{array}{l} \text{CO} \text{---} \text{NH} \\ \text{CHMe} \cdot \text{CO} \end{array}$ , is obtained,

which crystallises from alcohol in colourless prisms softening at  $165^\circ$  and melting at  $168^\circ$ . From the mother liquors of this amide, crystals of *dimethylfumaramide* melting at  $215^\circ$  may be obtained. When the imide is hydrolysed with barium hydroxide and the solution acidified with sulphuric acid and evaporated, the corresponding *anhydride*,  $\text{NH}_2\cdot\text{CMe} \begin{array}{l} \text{CO} \text{---} \text{O} \\ \text{CHMe} \cdot \text{CO} \end{array}$ , is obtained; it melts at  $164\text{--}165^\circ$ ,

dissolves readily in water, but is insoluble in ether, forms monoclinic prismatic crystals [ $a:b:c = 0.7955:1:0.5914$ ;  $\beta = 64^\circ 18'$ ], and when boiled for some time with water yields a small quantity of a crystalline compound which does not melt even at  $330^\circ$ , and is probably the corresponding acid. An *acid barium salt*,  $\text{C}_{12}\text{H}_{18}\text{O}_7\text{Ba}$ , is obtained when the anhydride is treated with one equivalent of barium hydroxide.

The original mother liquors from the imide, when repeatedly concentrated in a desiccator, yield hard, colourless crystals of *dimethylmaleamide*, which softens at  $155^\circ$ , melts at  $161^\circ$ , and when hydrolysed with barium hydroxide yields a compound free from nitrogen, together with a crystalline compound containing nitrogen.

When the mother liquor from the amide is extracted with ether, it yields a substance identical with the dimethylmaleimide obtained by Weidel and Brix (*Abstr.*, 1882, 1304). From the results of molecular weight determinations, the substance must have the simple formula, although when hydrolysed with barium hydroxide only half the nitrogen is evolved as ammonia. Among the products of hydrolysis is an *acid* isomeric with dimethylmaleic acid; this crystallises in nodular masses composed of small prisms, melts at  $151\text{--}152^\circ$ , and is regarded by the author as the hitherto unknown dimethylfumaric acid. The same acid

is formed when aminodimethylsuccinic anhydride is treated with methyl iodide and alkali. This conversion of dimethylmaleic anhydride into dimethylfumaric acid is analogous to Körner and Menozzi's conversion of maleic anhydride into fumaric acid. J. J. S.

**Formation of Oxalacetic Acid by Oxidation with Potassium Permanganate in Alkaline Solution.** By RUDOLPH FITTIG (*Ber.*, 1900, 33, 1295—1296).—By following the procedure of Fenton and Jones (*Trans.*, 1900, 77, 77), the author is now able to obtain appreciable quantities of oxalacetic acid by the oxidation of tereconic acid with potassium permanganate in alkaline solution (compare *Abstr.*, 1899, i, 418). R. H. P.

**[Tartar] Emetics.** By G. BAUDRAN (*Ann. Chim. Phys.*, 1900, [vii], 19, 536—574).—The most convenient method of preparing tartar emetics having definite physical and chemical properties is by treating the substance produced by the interaction of tartaric acid with a hydrated sesquioxide, prepared in the cold, with a solution of a normal alkali tartrate. Ordinary tartar emetic, when prepared in this way, dissolves in 25 parts of water at 25°, and in 3 parts at 100°, and has  $[\alpha]_D + 136^{\circ}4'$ .

Bismuth hydrated oxide,  $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , readily combines with tartaric acid, yielding *bismuthotartaric acid*,  $\text{C}_4\text{H}_5(\text{BiO})\text{O}_6 \cdot \text{H}_2\text{O}$ ; this substance crystallises in prismatic needles, dissolves in 228 parts of water, and has  $[\alpha]_D + 93^{\circ}40'$ . The corresponding *emetic*,  $\text{C}_4\text{H}_4(\text{BiO})\text{KO}_{6\frac{1}{2}} \cdot \text{H}_2\text{O}$ , resembles the antimony analogue, and has  $[\alpha]_D + 47^{\circ}35'$ ; unlike the product obtained by Schwarzenberg, it is not decomposed by water.

The *manganese emetic*,  $\text{C}_4\text{H}_4(\text{MnO})\text{KO}_{6\frac{1}{2}} \cdot \text{H}_2\text{O}$ , obtained by dissolving the hydrate  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$  in potassium tartrate, and then adding the necessary amount of tartaric acid, separates in pink crystals, and has  $[\alpha]_D + 23^{\circ}20'$ .

*Borotartaric acid*,  $\text{B}(\text{C}_4\text{H}_5\text{O}_6)_3 \cdot 3\text{H}_2\text{O}$ , produced by the action of tartaric acid (3 mols.) on orthoboric acid (1 mol.), forms very soluble, prismatic crystals, and has  $[\alpha]_D + 26^{\circ}30'$ . The *potassium salt* (boron emetic),  $\text{B}(\text{C}_4\text{H}_4\text{KO}_6)_{\frac{3}{2}} \cdot \frac{1}{2}\text{H}_2\text{O}$ , prepared either by the general method or by neutralising the preceding acid with potassium hydroxide (3 mols.), is soluble in 16 parts of boiling water, and has  $[\alpha]_D + 20^{\circ}50'$ .

*Ferritartaric acid*,  $\text{Fe}_2(\text{C}_4\text{H}_5\text{O}_6)_6 \cdot 10\text{H}_2\text{O}$ , is obtained in red, prismatic crystals when ferric hydroxide is treated with a cold solution of tartaric acid (6 mols.), and has  $[\alpha]_D + 60^{\circ}$ ; when heated at 100°, it loses water and becomes greenish-yellow; its neutral solutions do not give iron reactions with potassium thiocyanate or ammonium hydrosulphide. *Potassium ferritartrate*,  $\text{Fe}_2(\text{C}_4\text{H}_4\text{KO}_6)_6 \cdot \text{H}_2\text{O}$ , prepared by methods similar to those employed for the borotartrate, forms yellow crystals, and has  $[\alpha]_D + 45^{\circ}$ ; the *ammonium salt* has  $[\alpha]_D + 49^{\circ}50'$ .

*Aluminotartaric acid*,  $\text{Al}_2(\text{C}_4\text{H}_5\text{O}_6)_6 \cdot 6\text{H}_2\text{O}$ , obtained like the corresponding ferric derivative, crystallises in prisms, dissolves in its own weight of water, and has  $[\alpha]_D + 20^{\circ}$ ; its *potassium salt*,  $\text{Al}_2(\text{C}_4\text{H}_4\text{KO}_6)_6 \cdot \text{H}_2\text{O}$ , has  $[\alpha]_D + 23^{\circ}20'$ .

*Chromotartaric acid*, like the aluminium compound, crystallises with  $6\text{H}_2\text{O}$ , and its *potassium salt* crystallises with  $11\text{H}_2\text{O}$ ; green and violet

modifications of these compounds have been obtained, the former being the more stable in the case of the salt, and the latter in that of the acid.  
G. T. M.

**General Observations on "Emetics."** By L. LÉON A. PRUNIER (*Bull. Soc. Chim.*, 1900, [iii], 23, 101—103).—A short account of Baudran's work (preceding abstract), with a view to the discussion of its theoretical significance.  
N. L.

**Some Racemic Substances.** By J. SCHLOSSBERG (*Ber.*, 1900, 33, 1082—1087).—By adding to saturated solutions of the following inactive salts or acids at 20° some of the corresponding *d*-salts or acids (in the case of tropic acid the *l*-acid), and finding that the amount dissolved was increased thereby, and that the solution acquired a slight optical activity, it was shown that the inactive substances in question exist at 20° as racemic compounds: sodium lithium racemate,  $C_4H_4O_6NaLi \cdot 2H_2O$  (*d*-tartrate,  $C_4H_4O_6NaLi \cdot H_2O$ ); potassium sodium racemate; ammonium lithium racemate (*d*-tartrate,  $C_4H_4O_6(NH_4)Li \cdot \frac{1}{2}H_2O$ ); potassium sodium racemate; inactive potassium pyrotartrate,  $C_5H_6O_6K_2 \cdot H_2O$ ; inactive sodium pyrotartrate,  $C_5H_6O_6Na_2 \cdot 6H_2O$ ; tropic acid; mandelic acid (compare Rimbach, *Abstr.*, 1899, i, 895).  
C. F. B.

**Preparation of Acetylacetone.** By LUDWIG KNORR (*Ber.*, 1900, 33, 1219).—Ethyl diacetylsuccinate, when boiled for 1 hour with 20 per cent. aqueous potassium carbonate, gives an 80 per cent. yield of acetylacetone; the latter boils at 191°, 178°, and 137° under pressures of 750, 500, and 150 mm. respectively. It has a sp. gr. 0.973 at 20°/4°,  $\mu_D$  1.428 at 20°, and a molecular refraction 30.14, that calculated for the keto-formula being 30.10, and for the enolic formula 31.98.  
W. A. D.

**Syntheses with Acetylacetone. I.** By THOMAS GRAY (*Ber.*, 1900, 33, 1220—1223).—Acetylacetone combines with diethyl oxalate in presence of sodium to form diethyl acetylacetonedioxalate (*diethyl decane- $\beta\delta\eta$ -tetrone- $\alpha\kappa$ -dicarboxylate*),

$CO_2Et \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$ , which crystallises from alcohol in nearly colourless, lustrous, rhombohedral leaflets, melts at 100—101°, and with alcoholic hydrazine hydrate yields symmetrical di-3-carboxethylpyrazyl-5-ethane [*ethyl ethane-bis-5-pyrazyl-3-carboxylate*],  $C_2H_4 \left( C \begin{smallmatrix} \text{CH} \cdot C \cdot CO_2Et \\ \text{NH} \cdot N \end{smallmatrix} \right)_2$ ; this

crystallises from alcohol in rhombohedral leaflets, melts at 198—199°, and, on hydrolysis, yields the corresponding dicarboxylic acid,  $C_{10}H_{10}O_4N_4$ , as a crystalline powder. The latter melts at 309—310°, and is thereby converted into 5-dipyrazylethane,  $C_2H_4 \left( C \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{NH} \cdot N \end{smallmatrix} \right)_2$ ,

which crystallises from dilute alcohol in spindle-shaped crystals, and melts at 150—151°; on oxidation with alkaline potassium permanganate, the acid yields pyrazole-3:5-dicarboxylic acid (Knorr and Macdonald, *Abstr.*, 1894, i, 543).

The alternative formula,  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CHAc}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , for the condensation product of acetylacetone with diethyl oxalate is excluded by the foregoing facts. W. A. D.

**Oxidation of Erythritol by the Sorbose Bacterium.** Production of Erythrulose, a new Sugar. By GABRIEL BERTRAND (*Compt. rend.*, 1900, 130, 1330—1333. Compare Abstr., 1898, i, 550, 556).—*Erythrulose*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , is produced by allowing a culture of the sorbose bacterium to develop in a decoction of yeast and erythritol; after three weeks, when the polyhydric alcohol is completely oxidised, the solution is freed from zooglea, neutralised with a solution of barium hydroxide, and evaporated under diminished pressure, the sugar being obtained as an uncrystallisable syrup. Like its lower homologue dihydroxyacetone, erythrulose readily reduces Fehling's solution, even in the cold, combines with sodium hydrogen sulphite, and is easily soluble in a mixture of alcohol and ether; it has a specific rotation  $+12^\circ$  and is non-fermentable. Its hydrazones, produced by the action of phenylhydrazine, bromophenylhydrazine, and phenylbenzylhydrazine in cold solutions, are all extremely soluble, and could not be isolated. In warm dilute acetic acid solutions, the osazones are formed; *phenylerythrulosazone*,  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4$ , crystallises in golden-yellow needles, melts at  $174^\circ$ , has a specific rotation  $+50^\circ$ , and is very soluble in alcohol and acetone; *p-bromophenylerythrulosazone*,  $\text{C}_{16}\text{H}_{16}\text{Br}_2\text{O}_2\text{N}_4$ , is somewhat less soluble than the preceding compound, and melts at  $194$ — $195^\circ$ . The new sugar is very stable towards aqueous solutions of bromine; its aldehydic isomerides (Wohl, this vol., i, 140), on the contrary, yield monobasic acids containing four carbon atoms. Further investigations are being conducted, with a view of ascertaining whether erythrulose belongs to the *d*- or the *l*-series, or whether it is a mixture containing unequal proportions of both modifications. G. T. M.

**Pentoses and Methylpentoses.** By SULEIMAN BEY (*Chem. Centr.*, 1900, i, 803—804; from *Zeit. klin. Med.*, 39, 305—312).—*Barium dixylosate*,  $\text{BaO}(\text{C}_5\text{H}_{10}\text{O}_5)_2$ , separates as a white, amorphous precipitate when a hot, saturated solution of barium hydroxide is added to an alcoholic solution of xylose, or when barium hydroxide is dissolved in a solution of xylose at the ordinary temperature, and the filtrate poured into 96 per cent. alcohol at  $0^\circ$ . The composition of this precipitate, unlike those similarly prepared from dextrose, levulose, sucrose, and lactose, is not dependent on the relative proportions of barium hydroxide, alcohol, or xylose. Xylose may be completely precipitated from aqueous solutions in this form, and its amount estimated with accuracy. On keeping, the dry compound gradually becomes canary-yellow, whilst the strontium salt, which is similarly prepared, turns reddish-yellow. Calcium dixylosate is not precipitated by alcohol from solutions containing less than 30 per cent., and arabinose and xylose behave in this respect like dextrose and sucrose. Barium and strontium diarabinoxates are prepared in a similar way to the dixylosates, but both compounds are very unstable. The barium pentosates are completely decomposed by carbon dioxide, the carbo-

hydrates being liberated in a state of purity, whilst, under similar conditions, only 3—5 per cent. of the corresponding saccharate is attacked. E. W. W.

**Compounds of Fructose (Lævulose) with the Haloid Salts of the Alkaline Earths; Oxidation of Fructose.** By ROBERT H. SMITH and BERNHARD TOLLENS (*Ber.*, 1900, 33, 1277—1285).—The compound,  $C_6H_{12}O_6 \cdot CaBr_2 \cdot 4H_2O$ , is obtained when bromine is added to an aqueous solution of lævulose in which precipitated calcium carbonate is suspended, and forms a white, crystalline mass; it can also be obtained from lævulose and calcium bromide, and is very soluble in water, but is not deliquescent. In water, it has at first a specific rotation  $[\alpha]_D + 40.25^\circ$  and a constant specific rotation  $[\alpha]_D - 36.54^\circ$ ; if, however, these values are recalculated according to the amount of lævulose in the solutions examined, values of  $[\alpha]_D$  are obtained practically coinciding with those for lævulose, thus showing that the additive compound is decomposed by water. The compound,  $(C_6H_{12}O_6)_2 \cdot CaCl_2 \cdot 2H_2O$ , is obtained in a similar manner, and has a specific rotation  $[\alpha]_D - 64.5^\circ$ . The compound,  $(C_6H_{12}O_6)_2 \cdot CaI_2 \cdot 2H_2O$ , forms a hard, deliquescent mass, and shows a constant specific rotation  $[\alpha]_D - 47.4^\circ$ . The compound,  $(C_6H_{12}O_6)_3 \cdot SrCl_2 \cdot 3H_2O$ , is very stable in air, and shows a constant specific rotation  $[\alpha]_D - 57.6^\circ$ . The compound,  $(C_6H_{12}O_6)_2 \cdot SrBr_2 \cdot 3H_2O$ , forms stable, transparent, tabular crystals, and shows a constant specific rotation  $[\alpha]_D - 49.9^\circ$ . The compound,  $(C_6H_{12}O_6)_3 \cdot (SrI_2)_2 \cdot 4H_2O$ , forms a very hard mass, and the compound,  $(C_6H_{12}O_6)_2 \cdot BaI_2 \cdot 2H_2O$ , is deliquescent. On mixing solutions of lævulose and these haloid salts, heat is generally developed, and 1 mol. of lævulose seems to replace 2 mols. of water of crystallisation.

The authors confirm Kiliani's statement (*Ber.*, 1882, 14, 2530) that lævulose, on oxidation with nitric acid, yields mesotartaric acid and small quantities of glycollic acid. R. H. P.

**Polarisation and Reducing Power of Sorbose.** By ROBERT H. SMITH and BERNHARD TOLLENS (*Ber.*, 1900, 33, 1285—1293).—The specific rotation of sorbose in aqueous solution can be calculated from the formula  $[\alpha]_D = -(42.65 + 0.047p + 0.00007p^2 - [t - 20]0.02)^\circ$ , where  $p$  is the percentage concentration and  $t$  the temperature.

It was found that sorbose would reduce far less Fehling's solution than the same weight of dextrose under equal conditions, and a formula is given showing the reducing power of sorbose. R. H. P.

**Variation of the Specific Rotation of Sucrose with the Temperature.** By OTTO SCHÖNROCK (*Zeit. Ver. Deut. Zuck.-Ind.*, 1900, 413—434).—An elaborate series of experiments leads to the following expression for the variation of the specific rotation of sucrose in solutions containing about 26 grams per 100 c.c. for temperatures lying between  $10^\circ$  and  $32^\circ$ .  $[\alpha]_D^t = [\alpha]_D^{20^\circ} - [\alpha]_D^{20^\circ} \cdot 0.000217 (t - 20)$ , where  $[\alpha]_D^t$  is the specific rotation at the temperature  $t$ . T. H. P.

**Stability of Sucrose Solutions.** By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, 130, 1261—1263. Compare this vol., i, 236).—A current of dry, sterilised air produces no alteration in a



sterilised aqueous solution of sucrose protected from light, even when the experiment is continued for a fortnight. If ordinary air is allowed to enter, the dissolved sugar rapidly becomes inverted; at the same time, moulds develop in the solution and fermentation sets in attended by the formation of ethyl alcohol and carbon dioxide. Acetaldehyde, glycol, glycerol, oxalic and succinic acids could not be detected in the fermented solution. G. T. M.

**Gum Tragacanth.** By ALBERT HILGER and W.-E. DREYFUS (*Ber.*, 1900, 33, 1178—1191).—Five different samples of gum tragacanth were found to contain 15.4—9.4 per cent. of water, and 3.1—2.7 of ash; also 15.1—22.4 of galactose (estimated as mucic acid), and 42—30 per cent. of arabinose (estimated as furfuraldehyde phenylhydrazone). The samples obtained by artificial incision of the plant contain the larger quantities of water and ash. A sample of vermicelli tragacanth ("Fadentragant") contained 4 per cent. of cellulose and 3 of starch; allowing for these, the tragacanth proper is found to have the composition of a polysaccharide,  $C_{11}H_{20}O_{10}$ , for which the name *bassorin* should be reserved; this is quite insoluble in water. When the gum is boiled for 30 hours with 2 per cent. sulphuric acid, arabinose can be isolated from the product, but no other crystalline substance; the mother-liquors, however, yield mucic acid on oxidation. When it is allowed to remain 2—3 days in 35 per cent. potassium hydroxide, and the alkaline solution precipitated with glacial acetic acid, *oxybassorin*,  $(C_{11}H_{20}O_{10})_2O$ , is obtained. If the alkaline solution is neutralised with dilute acetic acid and precipitated with alcohol, a *potassium* derivative of oxybassorin is obtained; this is soluble in water and yields insoluble *copper* and *silver* derivatives by double decomposition. These compounds do not give the usual reactions of the metals, and cannot be regarded as true salts. The potassium derivative has the character of a simple sugar; it is strongly dextrorotatory, and reduces Fehling's solution and ammoniacal silver solution, but not Soldani's reagent, and does not restore the colour to magenta solution decolorised with sulphurous acid. Sodium amalgam reduces an alkaline solution of oxybassorin to an optically inactive substance without reducing properties. C. F. B.

**Some New Tellurium Compounds.** By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1900, 22, 136—141).—Tellurium tetrabromide and tetrachloride readily unite with the corresponding halogen salts of both aliphatic and aromatic amines to form well-crystallised double salts of the composition  $(B'HBr)_2TeBr_4$  and  $(B'HCl)_2TeCl_4$ . The bromides are invariably red, and the chlorides yellow. They are all soluble in dilute acids and in alcohol, but are decomposed by pure water with the formation of hydrated tellurium dioxide. The following salts are described: the *telluribromides* of ethylamine, trimethylamine, aniline, pyridine, and quinoline, and the *tellurichlorides* of methylamine, ethylamine, aniline, pyridine, and quinoline.

A solution of tellurium dioxide in halogen acids also yields a precipitate with most of the alkaloids. E. G.

**Bewad's Triethylamine Oxide.** By ARTHUR LACHMAN (*Ber.*, 1900, 33, 1030—1034. Compare Abstr., 1899, i, 326).—The author has prepared further quantities of Bewad's triethylamine oxide (Abstr., 1888, 112, 1127) by the method previously described, and from a study of the reactions of the compound, comes to the conclusion that it resembles the hydroxylamines, especially diethylhydroxylamine, and its isomerism with Dunstan and Goulding's compound thus becomes even more difficult to explain.

The hydrochloride forms large, extremely hygroscopic crystals. The base, when boiled at atmospheric pressure, undergoes partial decomposition; it reacts with methyl iodide, iodine being liberated, and triethylamine hydriodide formed. No condensation products could be obtained with either aniline or phenylhydrazine. It readily reduces dichromate, permanganate, Fehling's solution, ammoniacal silver nitrate, and sodium nitrite.

J. J. S.

**Diethylhydroxylamine.** By ARTHUR LACHMAN (*Ber.*, 1900, 33, 1022—1030. Compare Dunstan and Goulding, *Trans.*, 1899, 75, 792).—In most syntheses with zinc alkyls, two alkyl groups can only be introduced into the molecule when 2 mols. of the reagent are employed. With diphenylnitrosamine, however, two ethyl groups are introduced, and diethylhydroxylamine is formed when only 1 mol. of zinc ethyl is employed. Dimethyl- and diethyl-nitrosamine, on the other hand, do not react with zinc ethyl. Special precautions are required in the isolation of the diethylhydroxylamine, for which the original must be consulted.

After extraction with ether, it is most readily purified by fractional distillation under about 100 mm. pressure, the yield being usually about 30 per cent. The pure base forms a colourless, oily liquid with a characteristic aromatic odour, boils at 47—49° under 15 mm., 79—80° under 100 mm., and 130—135° under 750 mm. pressure, but with some decomposition in the last case, has a sp. gr. 0.8784 at 15°/15°, and dissolves readily in all solvents with the exception of light petroleum. Its aqueous solution precipitates lead, copper, zinc, and aluminium salts, but not those of magnesium, cobalt, or nickel, and in addition has strong reducing properties. The *hydrochloride*,  $C_4H_{11}ON \cdot HCl$ , forms white, crystalline scales, melting indefinitely at 55—65°. *Triethylhydroxylammonium iodide*,  $OH \cdot NEt_3I$ , formed by the direct union of ethyl iodide and diethylhydroxylamine, crystallises in needles, softens at 40°, but has no fixed melting point; it is extremely hygroscopic, and is insoluble in benzene, ether, or light petroleum; when reduced, it yields triethylamine, and when heated triethylamine, triethyloxamine, iodine, and water.

Triethyloxamine platinichloride (compare Dunstan and Goulding, *loc. cit.*) crystallises from water with  $2H_2O$ .

J. J. S.

**Quinquevalent Nitrogen.** By ARTHUR LACHMAN (*Ber.*, 1900, 33, 1035—1040. Compare Abstr., 1898, i, 400).—The following are the more important generalisations brought forward by the author.

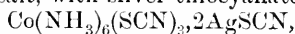
No quinquevalent nitrogen derivatives are known in which the five radicles are of the same chemical nature; one or more of the radicles

must be of an opposite chemical nature, but not too pronounced. An increase of temperature tends to convert a quinque- into a ter-valent derivative; this is most pronounced when two of the five radicles are of opposite chemical nature to the remaining three.

Certain nitro-derivatives, for example, nitrobenzene, contain ter-valent nitrogen; others, for example, nitroethane, quinquevalent nitrogen.

J. J. S.

**Ammonio-cobalt Thiocyanates.** By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1900, 240—244).—*Luteocobalt thiocyanate*,  $\text{Co}(\text{NH}_3)_6(\text{SCN})_3$ , is obtained by adding barium thiocyanate to a solution of luteocobalt sulphate containing a small quantity of sulphuric acid, and evaporating the filtrate in a vacuum over sulphuric acid; it crystallises in orange-yellow, lustrous tablets, is decomposed by hot water, and can be recrystallised from a solution of magnesium thiocyanate. The *double salt*, with mercury thiocyanate,  $\text{Co}(\text{NH}_3)_6(\text{SCN})_3 \cdot 2\text{Hg}(\text{SCN})_2$ , obtained by heating a solution of the preceding salt with mercury thiocyanate, crystallises in beautiful, golden leaflets, is decomposed by water, and can be recrystallised from a solution of ammonium thiocyanate. The *double salt*, with silver thiocyanate,



crystallises in lustrous, yellow leaflets, and is decomposed by water. The *double salt*, with platinum thiocyanate, is an orange-yellow, micro-crystalline precipitate, and is decomposed by hot water. These double salts do not correspond in composition to those obtained from luteocobalt chloride or luteochromium chloride and mercury chloride, but are analogous to the complex fluorides,  $\text{Co}(\text{NH}_3)_6\text{Fl}_3 \cdot 2\text{SiFl}_4$ , &c., previously described by Miolati and Rossi (*Abstr.*, 1898, ii, 222).

E. C. R.

**Double Thiocyanates.** By ARTHUR ROSENHEIM and ROBERT COHN (*Ber.*, 1900, 33, 1111—1114).—*Mercury bromothiocyanate*,  $\text{HgBr} \cdot \text{SCN}$ , crystallises in beautiful needles and is insoluble in water, but dissolves unchanged in hot alcohol.

*Ammonium* and *barium* salts of the type  $\text{M}'\text{Hg}(\text{SCN})_3$ , and *potassium*, *sodium*, *barium*, and *copper* salts of the type  $\text{M}'_2\text{Hg}(\text{SCN})_4$  were prepared, the former class being sparingly, the latter easily, soluble in water.

Cobalt yields salts of the type  $\text{M}'_2\text{Co}(\text{SCN})_4$ , which form dark blue crystals, and are easily soluble in water; the *potassium* and *ammonium* (each with  $4\text{H}_2\text{O}$ ) and the *sodium* and *barium* (each with  $8\text{H}_2\text{O}$ ) salts were analysed. The corresponding crystalline *nickel* salts are green; the *sodium* compound,  $2\text{NaSCN} \cdot \text{Ni}(\text{SCN})_2 \cdot 8\text{H}_2\text{O}$ , has a normal, but the *potassium* salt,  $4\text{KSCN} \cdot \text{Ni}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ , an abnormal, composition. It is noteworthy that, in alcoholic solution, the cobalt of the cobalt salts is present in the anion  $\text{Co}(\text{SCN})_4$ , and is deposited on the anode; the nickel of the nickel salts, however, is deposited at the cathode.

The crystalline *aluminium* salt,  $\text{Al}(\text{SCN})_3 \cdot \text{K}_6 \cdot 4\text{H}_2\text{O}$ , prepared by the action of thiocyanic acid on freshly precipitated aluminium hydroxide in presence of potassium thiocyanate, is easily soluble in water; the corresponding chromium salt (Rösler, *Annalen*, 1867, 141, 185) can be prepared in a similar way.

W. A. D.

**New Organo-metallic Compounds of Magnesium and their Application to the Synthesis of Alcohols and Hydrocarbons.** By V. GRIGNARD (*Compt. rend.*, 1900, 130, 1322—1324. Compare Barbier, *Abstr.*, 1899, i, 323).—Magnesium turnings act on methyl iodide with extreme slowness, but if anhydrous ether is added a vigorous reaction sets in and the metal dissolves completely, giving rise to a clear, almost colourless, liquid. On distilling off the ether, a grey, semi-crystalline residue is obtained which rapidly deliquesces with an appreciable rise of temperature. When an aldehyde or ketone is added to the ethereal solution, it readily combines with the magnesium compound  $\text{MgMeI} + \text{RCHO} = \text{R}\cdot\text{CHMe}\cdot\text{O}\cdot\text{MgI}$ , and the product, when treated with dilute acid, furnishes a secondary or tertiary alcohol,  $\text{RCHMe}\cdot\text{O}\cdot\text{MgI} + \text{H}_2\text{O} = \text{MgI}\cdot\text{OH} + \text{R}\cdot\text{CHMe}\cdot\text{OH}$ , the yield being about 70 per cent. of the theoretical. The reaction is perfectly general for all alkyl iodides and bromides up to the  $\text{C}_5$  series. A similar result is produced with benzyl chloride, but the yield is much less owing to the formation of dibenzyl. The following alcohols have been prepared for the first time.

*Phenylisobutylcarbinol*,  $\text{C}_4\text{H}_9\cdot\text{CHPh}\cdot\text{OH}$ , from benzaldehyde and *isobutylbromide*, is a colourless, viscid liquid boiling at  $122^\circ$  under 9 mm. pressure.

*Phenyltrimethylcarbinol*,  $\text{CMe}_3\text{Ph}\cdot\text{OH}$ , from acetophenone and methyl iodide, is a colourless liquid with an agreeable odour; it boils at  $93\text{--}95^\circ$  under 10 mm. pressure.

*Benzyltrimethylcarbinol*,  $\text{CH}_2\text{Ph}\cdot\text{CMe}_3\cdot\text{OH}$ , from acetone and benzyl bromide, is a colourless, somewhat viscid liquid boiling at  $103\text{--}104^\circ$  under 10 mm. pressure.

When unsaturated aldehydes or ketones are employed which have their double linkings near the carbonyl group, then the alcohols which are formed at first become dehydrated and olefine hydrocarbons are produced.

*$\beta\delta$ -dimethyl- $\Delta^{\beta\delta}$ -pentadiene*,  $\text{CMe}_3\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$ , obtained from mesityl oxide and methyl iodide, boils at  $92\text{--}93^\circ$  under 750 mm. pressure. G. T. M.

**Chemistry of Mercury. II. Mercuric Salts of Ketonic Acids, and Conversion of these into Mercurioketonic Acids.** By HEINRICH LEY (*Ber.*, 1900, 33, 1010—1014. Compare *Abstr.*, 1899, ii, 485).—*Mercuric levulate*,  $\text{Hg}(\text{C}_5\text{H}_7\text{O}_3)_2$ , crystallises in characteristic silvery plates, and has the molecular conductivity  $\mu$  7.88 ( $v=64$ ),  $\mu$  12.54 ( $v=128$ ). Aqueous sodium hydroxide added to a solution of the salt produces a yellow precipitate of mercuric hydroxide, which dissolves in excess of the reagent, yielding a solution from which acetic acid precipitates a white, gelatinous mass; this is apparently a mixture of the *mercurilevulic* acids,  $\text{C}_5\text{H}_6\text{O}_3\text{Hg}$  and  $\text{C}_5\text{H}_4\text{O}_3\text{Hg}_2$ , and yields levulic acid when decomposed by hydrogen sulphide.

A similar reaction is given by pyruvic,  $\beta$ -acetoisobutyric, and acetonedicarboxylic acids. Crotonic acid also yields a mercuri-compound, the formation of which is probably favoured by the presence of the ethylene linking. A. H.

**Mercarbide,  $C_2H_2O_4Hg_6$ .** By KARL A. HOFMANN (*Ber.*, 1900, 33, 1328—1339. Compare *Abstr.*, 1898, i, 635).—The compound  $OHg_2 \cdot C(Hg \cdot OH) \cdot C(Hg \cdot OH) \cdot OHg_2$ , formerly described (*loc. cit.*) by the author as an oxymerccarbide, is now proved to be a derivative of ethane; it is best prepared by the action of yellow mercuric oxide and aqueous alkali on ethyl alcohol; the base is also obtained, although in smaller yield, if acetaldehyde, propyl alcohol, allyl alcohol, amyl alcohol, cellulose, starch, or sucrose are used in place of ethyl alcohol. It differs from all other organic mercury compounds by its great stability towards hot concentrated alkali and acids, permanganate, chromic acid, alkali hypochlorites and hypobromites, nitrohydrochloric acid, sulphurous acid, hydroxylamine, and dilute hydrazine solution; at high temperatures, it loses water, and an orange-red, explosive compound,  $C_2O_3Hg_6$  (?), is formed. By heating the base (1 mol.) with ethyl iodide (6 mols.) in ethereal solution, the *iodide*,  $C_2I_6Hg_6$ , is obtained as a crystalline compound of an intense reddish-yellow colour, insoluble in water, alcohol, or ether. The mercarbide acts on aqueous potassium haloids with liberation of alkali; with potassium chloride, a *chloride*,  $C_2O_2Cl_2Hg_6$ , is formed, and this, with potassium iodide solution, gives an intense orange-yellow, basic *iodide*. The base forms a white *perchlorate*,  $C_2O_2Hg_6(ClO_4)_2$ , which, when heated or rubbed, explodes and emits a green light. With sodium hydrogen sulphite solution, the mercarbide gives a bright yellow *substance*, which is turned grey by the action of light, and from which the base is regenerated by heating with nitric acid and then with sodium hydroxide. On digesting the mercarbide *nitrate*,  $C_2O_3Hg_6(NO_3)_2$ , with ammoniacal ammonium nitrate solution, the *compound*,  $C_2O_3Hg_6(NH_3)_2(NO_3)_2$ , is obtained, whilst the chloride gives a yellowish-white *powder* of the composition  $C_2O_2Cl_2Hg_6(NH_3)_2$  when treated with ammoniacal ammonium chloride solution. Hydrogen sulphide gives, with the mercarbide, a white *sulphide*, and hydrazine hydrate slowly reduces the base, nitrogen and ethane being evolved and mercury deposited.

[With E. EICHWALD.]—The yellow, slightly explosive *cyanide*,  $C_2Hg_4(CN)_2$  (*loc. cit.*), obtained by the action of potassium cyanide on the nitrate of the mercarbide, is not acted on by ammonia, but with hydrogen sulphide gives a white *compound*,  $C_2H_2Hg_4S_2$ , insoluble in water, alcohol, or ether; with hot 10 per cent. hydrochloric acid, the cyanide yields the *chloride*  $(CHCl_2Hg_2)_2$ . On boiling the latter with concentrated hydrochloric acid, it is converted into a volatile, strongly-smelling, poisonous compound,  $C_2H_4Cl_2Hg_2$ , which crystallises in colourless, rectangular leaflets, showing very slight double refraction, and melting at about  $173^\circ$ ; it is readily soluble in alcohol, ether, or water, and from its aqueous solution potassium iodide precipitates slender, white needles of an *iodide*, which crystallises from alcohol or ether in quadratic, optically inactive plates; with the hydrochloric acid solution of the chloride, hydrogen sulphide gives a *sulphide* separating from alcohol in white crystals.

The action of mercuric oxide and alkali on alcohol yields, besides mercarbide, an intermediate product, *trimercuriacetic acid*; it exists

in two modifications, one soluble and the other insoluble in alkali, and gives a *nitrate*,  $\text{NO}_3\text{Hg}\cdot\text{C}(\text{Hg}\cdot\text{OH})_2\cdot\text{CO}_2\text{H}$ .

[With W. BOSCH.]—On heating the insoluble trimercuriacetic acid with sodium ethoxide and alcohol, it is partly converted into the soluble form, and partly resolved into the mercarbide and oxalic acid; an alkaline solution of the acid is decomposed by permanganate, carbon dioxide being evolved, and the mercarbide formed; heating with mercuric oxide and sodium hydroxide solution also converts the trimercuriacetic acid into mercarbide.

[With JULIUS SAND.]—On extracting the product of the action of methyl alcoholic potash and mercuric oxide on potato-starch with nitric acid, besides the nitrate of the mercarbide, another *nitrate* of the composition  $\text{C}_3\text{H}_6\text{O}_3\text{Hg}_2\cdot\text{NO}_3$  is obtained, whilst in the case of sucrose, a somewhat similar *compound* of the formula  $\text{C}_3\text{H}_6\text{O}_6\text{Hg}_4\cdot\text{NO}_3$  is formed.

T. H. P.

**Behaviour of Mercuric Salts towards Olefines.** By KARL A. HOFMANN and JULIUS SAND (*Ber.*, 1900, **33**, 1340—1353).—By the action of ethylene on solutions of mercuric salts, compounds of the following kinds are obtained. 1. Ethenemercury salts,  $\text{CH}_2\cdot\text{CH}\cdot\text{HgX}$ . 2. Ethanolmercury salts,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgX}$ . 3. Ethyl ether mercury salts,  $\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{HgX})_2$ . 4. Polymerised ethenemercury salts,  $(\text{C}_2\text{H}_3\text{HgX})_n$ . The formation of all these compounds is explained on the supposition that the mercury salt  $\text{HgX}_2$  splits up into the ions  $\text{X}$  and  $\text{HgX}$ , which then combine with the ethylene, converting it into the saturated compound  $\text{XHg}\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$ . If this then loses the elements of hydrogen haloid, ethenemercury salts are obtained, whilst if it undergoes hydrolysis, ethanolmercury salts result; if the hydrolysis is only partial, condensation of the product of hydrolysis and the original compound, with loss of hydrogen haloid, gives rise to compounds of type 3. Strong acids, especially hydrochloric, readily decompose all these compounds into ethylene and mercury salt.

On passing ethylene into aqueous mercuric chloride, the *double salt*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgCl}\cdot\text{HgCl}_2$ , is precipitated, together with fine spangles of the compound  $\text{C}_6\text{H}_{10}\text{O}_4\text{Cl}_4\text{Hg}_4$ , which is the *chloride* corresponding with the *sulphate*,  $\text{C}_6\text{H}_{10}\text{O}_{12}\text{S}_2\text{Hg}_4$ , obtained by precipitating mercuric sulphate solution by means of ethylene. The double chloride is only slightly soluble in water, but crystallises from alcohol in brilliant plates; it is decomposed by potassium cyanide or strong acids (not acetic), whilst hydrogen sulphide slowly precipitates all the mercury. Potassium hydroxide solution precipitates half the mercury as oxide, and by passing carbon dioxide into the alkaline solution the free ethanol derivative is obtained. The latter is best prepared by adding potassium hydroxide to mercuric nitrate solution until a precipitate persists, ethylene being then passed through until the liquid is clear; more alkali is added, and ethylene again passed through the solution, this process being repeated until a clear alkaline liquid remains. To this, potassium chloride or bromide is added in the proportion of 1 mol. to each atom of mercury present, the passage of carbon dioxide through the liquid then causing the precipitation of

the crystalline ethanolmercury salt. The *chloride*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgCl}$ , melts at  $155^\circ$ , and the *bromide* at  $158^\circ$ . The latter, which forms with ammonia a crystalline compound,  $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{HgBr}\cdot\text{NH}_3$ , melting at  $150^\circ$ , is oxidised by bromine in alkaline solution to *monobromomercuri-acetic acid*,  $\text{HgBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which separates as a white precipitate, gradually becoming crystalline. The last-named acid, which is obtained in better yield by the action of bromine on an alcoholic solution of mercuric bromide, does not give up its bromine when treated with alkali, nor is it decomposed by 20 per cent. nitric acid, dilute hydrochloric acid, or ammonia, but the addition of potassium iodide converts it into a yellow *iodo-compound*.

The addition of potassium iodide to the solution of ethylene in gradually neutralised mercuric nitrate gives rise, not to an ethanol-derivative, but to *ethenemercury iodide*,  $\text{CH}_2\cdot\text{CH}\cdot\text{HgI}$ , which separates from methyl alcohol in beautiful, silvery plates melting at  $147^\circ$ ; it is readily soluble in hot alcohol, and suffers decomposition by the action of hydrochloric acid or potassium cyanide. On boiling with mercuric oxide and caustic potash, it is converted into the white dimercuriacetic acid insoluble in alkali. The iodide is readily dissolved by sodium ethoxide, or by an aqueous or alcoholic solution of an equivalent quantity of potassium hydroxide, whilst it is decomposed, with formation of mercuric iodide and an olefine, by the action either of methyl iodide or of iodine in presence of water.

*Ethenemercury nitrate*,  $\text{CH}_2\cdot\text{CH}\cdot\text{HgNO}_3$ , obtained by the action of methyl alcoholic silver nitrate on ethanolmercury chloride, separates in spherical aggregates of thin, white, sparkling, doubly-refracting leaflets, which, on heating, give a slight explosion with evolution of reddish vapour. It is readily soluble in water, and the addition of a little dilute hydrochloric acid to the aqueous solution precipitates ethanolmercury chloride, which is decomposed by excess of acid.

*Ethanolmercury sulphide*,  $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Hg})_2\text{S}$ , is a white, crystalline substance, and the corresponding *hydrosulphide*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgSH}$ , crystallises from water in beautiful spangles.

*Ethyl ether mercury chloride*,  $\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{HgCl})_2$ , forming a white, granular, crystalline precipitate melting indefinitely at about  $190^\circ$ ; the *bromide*,  $\text{C}_2\text{H}_5\text{OBr}\cdot\text{Hg}_2$ , forming a fine, white, crystalline powder, and the *carbonate*,  $\text{C}_4\text{H}_8\text{OHg}_2\cdot\text{CO}_3$ , were also prepared.

A *polymeric ethenemercury iodide*,  $(\text{C}_2\text{H}_3\text{IHg})_n$ , separating from hot dilute alkali solution in fine spangles melting at  $161^\circ$ , and a *sulphide*,  $(\text{C}_2\text{H}_3\text{Hg})_2\text{S}$ , were also obtained.

T. H. P.

**Action of Propylene and Butylene on Mercuric Salts.** By JULIUS SAND and KARL A. HOFMANN (*Ber.*, 1900, 33, 1353—1358).—Although the action of ethylene on mercuric salts gives rise to four distinct classes of compounds (see preceding abstract), with propylene, only propanolmercury salts are obtained, whilst with isobutylene both butanolmercury salts and *isobutylmercury* salts are formed.

*Propanolmercury iodide*,  $\text{OH}\cdot\text{C}_3\text{H}_6\cdot\text{HgI}$ , crystallises from ether in long, slender needles melting at  $68^\circ$ ; it is readily soluble in alcohol or ether. The *bromide*, when crystallised from a mixture of alcohol

and ether, melts at  $76^{\circ}$ , and the *chloride* crystallises from ether in prisms melting at about  $53^{\circ}$ .

*Butanolmercury bromide*,  $\text{OH}\cdot\text{C}_4\text{H}_9\cdot\text{HgBr}$ , crystallises from benzene in small, shining prisms melting at  $66^{\circ}$ , and gives with ammonia a white *precipitate* of the composition  $\text{OH}\cdot\text{C}_4\text{H}_9\cdot\text{HgBr}\cdot\text{NH}_3$ ; the *chloride* melts at  $52^{\circ}$ . On attempting to prepare the iodide, *butenemercury iodide*,  $\text{C}_4\text{H}_7\text{IHg}$ , is obtained which separates from benzene or carbon disulphide in beautiful, colourless prisms, and is soluble in ether.

From neutral mercuric sulphate solutions, *isobutylene* precipitates an intensely yellow powder of the composition  $\text{C}_4(\text{OH})_6\text{Cl}_4\text{Hg}_{10}\text{H}_2\text{O}$ .

T. H. P.

**Action of Allyl Alcohol on Mercuric Salts.** By JULIUS SAND and KARL A. HOFMANN (*Ber.*, 1900, 33, 1358—1364).—In acid solutions, the action of allyl alcohol on mercuric salts gives rise to allenemercury salts,  $\text{XHg}\cdot\text{C}_3\text{H}_3$ , which, in presence of alkali, take up water and pass into propenolmercury compounds,  $\text{XHg}\cdot\text{C}_3\text{H}_4\cdot\text{OH}$ .

*Allenemercury nitrate*,  $\text{CH}_2\text{:C:CH}\cdot\text{HgNO}_3$ , is almost insoluble in water or organic solvents, but dissolves readily in dilute aqueous caustic alkali; on heating, it explodes with a large flame. It is not decomposed by potassium cyanide, but is slowly attacked by boiling 10 per cent. hydrochloric acid. The corresponding *hydrogen sulphate*,  $\text{CH}_2\text{:C:CH}\cdot\text{HgHSO}_4$ , separates as a mass of colourless crystals from a mixture of allyl alcohol with a solution of mercuric sulphate in dilute sulphuric acid. A *double* compound of allenemercury chloride with mercuric chloride,  $\text{HgCl}_2 + 2\text{C}_3\text{H}_3\cdot\text{HgCl}$ , separates from a mixture of aqueous mercuric chloride and allyl alcohol as a white, flocculent precipitate. If allyl alcohol is left for some time in contact with mercuric nitrate solution, the addition of water to the filtrate from the allenemercury nitrate precipitates a yellowish-white *nitrate*,



which, with hydrochloric acid, yields calomel and an odour of acrylic acid.

*Propenolmercury chloride*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH:CH}\cdot\text{HgCl}$ , forms a fine, white, crystalline precipitate, the *bromide* a heavy, white, crystalline powder, and the *iodide* fine spangles. *Propenolmercury cyanide*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH:CH}\cdot\text{HgCN}$ , forming a thick, white precipitate, the *sulphide*, and a *basic carbonate* were also prepared. Most of these salts are soluble in ammonia solution, and all dissolve in a solution of potassium hydroxide containing 1 mol. of the base for every atom of mercury present. They cannot be separated into their components by hydrochloric acid, as the strength of acid necessary decomposes allyl alcohol. The salts are oxidised by permanganate, but oxalic acid is the only product identified.

T. H. P.

**Action of Cyanogen Bromide and Aluminium Chloride on Benzenoid Hydrocarbons and Phenol Ethers.** By ROLAND SCHÖLL and WILHELM NÖRR (*Ber.*, 1900, 33, 1052—1058).—When cyanogen bromide acts on benzenoid hydrocarbons in presence of aluminium chloride, the principal products are cyanidins, whilst the



simple nitriles and brominated hydrocarbons are formed only in small quantities. In the case of anisole, however, the product consists for the most part of anisonitrile and *p*-bromoanisole (compare Friedel and Crafts, *Ann. Chim. Phys.*, 1884, [vi], 1, 528).

In these reactions, it is always the hydrogen in the para-position to a group already present which suffers replacement, and in the case of *p*-xylene and *p*-cymene, in which this is impossible, action does not occur.

Benzene and cyanogen bromide react in presence of aluminium chloride at 50°, yielding considerable quantities of cyaphenin. As the latter substance is not formed by the action of aluminium chloride on benzonitrile, it follows that it results from the action of benzene on the cyanuric bromide which is formed in the first instance.

*Cyan-o-xylins*,  $C_{27}H_{27}N_3$  ( $Me_2:C = 1:2:4$ ) is formed from *o*-xylene. It crystallises from benzene in small needles which sinter at 204° and melt and partially decompose at 210°. It yields *p*-xylic acid when heated at 220° with hydrochloric acid. *Cyan-m-xylins*,  $C_{27}H_{27}N_3$  [ $Me_2:CN = 1:3:4$ ], from *m*-xylene, crystallises from hot acetone in colourless leaflets melting at 154–155°. A. L.

**Law Governing the Elimination of Halogens from the Benzene Ring.** By AUGUST KLAGES and C. LIECKE (*J. pr. Chem.*, 1900, [ii], 61, 307–329).—A long series of experiments show that the presence of an alkyl group in the ortho- or para-position in the benzene ring has an equal effect on the elimination of a halogen, whilst one in the meta-position has much less influence, and that two alkyl groups in the diortho-positions or the orthopara-positions have a much greater influence than in the dimeta-positions. Alkyl groups, therefore, exercise an influence on chemical reactions, not only in the ortho- and diortho-positions, but also in the orthopara-positions. The introduction and elimination of a halogen group is more easily effected from homologues of benzene than from benzene itself. A similar law holds good for hydroxy-compounds; for example, *o*- and *p*-iodophenols are much more easily converted by hydrogen iodide into phenol than *m*-iodophenol.

The following new compounds are described: *m*-chloroiodobenzene, which boils at 230°; 3-iodo-*o*-xylene, which is a colourless oil boiling at 125–126° under 15 mm. pressure; 2-iodo-*m*-xylene, which is an oil boiling at 228–230°, and volatile with steam; 2-iodo-*p*-xylene, which boils at 229°. R. H. P.

**Formation of Tri-substituted from Di-substituted Benzene Derivatives.** By ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 478–480).—Benzoic acid, when nitrated at 0°, yields the three mononitro-compounds in the following proportions: 18.5, 80.2, and 1.3 per cent. for the ortho-, meta-, and para-isomerides respectively (Abstr., 1899, i, 759). The three dinitrobenzenes are all produced by the direct nitration of nitrobenzene at 0°, the relative amounts of the ortho-, meta-, and para-derivatives being respectively 6.4, 93.5, and 0.1 per cent.

In the nitration of the three nitrobenzoic acids, the entering radicle

is subjected to the joint influence of the two groups already present in the molecule. For example, in *o*-nitrobenzoic acid, the positions 3, 4, 5, and 6 are still unoccupied, and considering each of these in turn, it is seen that if the carboxyl group alone were present, 80.2 per cent. of the product would contain the entering group in position 3, whereas only 6.4 per cent. of the whole would have this orientation if the influence of the nitro-group alone is taken into account; the product of these two percentages, 504 ( $= 6.4 \times 80.2$ ), is taken as the numerical expression of the tendency to form the 2:3-dinitrobenzoic acid, the corresponding factors for the 2:4-, 2:5-, and 2:6-isomerides being 100, 8, and 1730 respectively. It is found that the 2:6-dinitrobenzoic acid, which corresponds with the highest factor, is the chief product of nitration. In *m*-nitrobenzoic acid, the coefficients for the unoccupied positions 2, 4, 5, and 6 are 118, 8, 7499, and 1.8 respectively; experiment shows that the 3:5-dinitrobenzoic acid, corresponding with the highest factor, is the sole product.

When *p*-nitrobenzoic acid is nitrated, the entering radicle may take up one or other of two positions; the factor for position 2 is 1730, whilst that for position 3 is 504; the mixture of dinitro-compounds actually produced consists mainly of the 2:4-compound, together with a small amount of the 3:4-isomeride.

A similar process of reasoning was adopted in predicting the constitution of the chloronitrobenzoic acids obtained by nitrating the three chlorobenzoic acids; these theoretical deductions are confirmed by Montagne's experiments (*Dissertation Leiden*, 1899). On nitrating *o*-chlorobenzoic acid, the main product is the 2-chloro-5-nitrobenzoic acid, accompanied by traces of the 2:3-acid; *m*-chlorobenzoic acid yields the 3:6-acid, together with small quantities of its isomerides, whilst *p*-chlorobenzoic acid gives rise to the 4:3-acid only.

G. T. M.

*m*-Xylylamine and *m*-Methylphenylethylamine. By F. SOMMER (*Ber.*, 1900, 33, 1073—1081).—The crude *m*-methylbenzylamine, obtained by reducing *m*-toluonitrile with alcohol and sodium, is easily purified by conversion into the corresponding *carbamide*,  $C_8H_9 \cdot NH \cdot CO \cdot NH_2$ , which crystallises in slender, white needles melting at 148°. The base regenerated from the latter is identical in all its properties with Brömme's *m*-xylylamine (*Abstr.*, 1888, 1295). The xylylamine prepared by Pieper from xylyl chloride (*Annalen*, 1869, 151, 129) was an impure form of the same substance.

The following new derivatives of the base have been prepared. The *hydrochloride*, colourless crystals melting at 208°; the *sulphate*, white leaflets melting and decomposing at 248°; the *mercurichloride*,  $(C_8H_9 \cdot NH_2 \cdot HCl)_2 HgCl_2$ , white leaflets melting at 184°.

The *m*-xylyl alcohol prepared from the base is identical with the substance obtained by Radziszewski and Wispek from ethyl *m*-xylyl-acetoacetate (*Abstr.*, 1882, 1283), and the corresponding aldehyde with that obtained from *m*-xylene by the Étard reaction. *m*-Xylylaldehyde-semicarbazone,  $C_8H_8 \cdot N \cdot NH \cdot CO \cdot NH_2$ , crystallises from dilute alcohol in slender needles, and melts at 216°.

*m*-Methylphenylethylamine,  $C_6H_4 Me \cdot CH_2 \cdot CH_2 \cdot NH_2$ , formed by re-

ducing *m*-xylyl cyanide with alcohol and sodium, is a colourless liquid, has powerful basic properties, and boils at 214—215° under 744 mm. pressure. The *hydrochloride* melts at 159°, and the *platinichloride*,  $(C_9H_{13}N)_2 \cdot H_2PtCl_6$ , is amorphous, and melts and decomposes at 243°. The *aurichloride* forms large, golden leaflets, which sinter at 73° and melt indefinitely at 85°. The *picrate* crystallises in beautiful, yellow leaflets and melts at 173°. The *carbamide*,  $C_9H_{11} \cdot NH \cdot CO \cdot NH_2$ , forms white leaflets and melts at 84°. The *benzoyl* derivative,  $C_9H_{11} \cdot NHBz$ , was obtained as a crystalline mass.

2-*m*-Methylphenylethylidihydroisindole,  $C_6H_4 \begin{smallmatrix} <CH_2 \\ >CH_2 \end{smallmatrix} N \cdot C_9H_{11}$ , is formed when *o*-xylylene dibromide is heated with *m*-methylphenylethylamine. The *platinichloride*,  $(C_{17}H_{19}N)_2 \cdot H_2PtCl_6$ , forms small, yellow crystals, which melt and decompose at 216°. A. L.

**Hydroxyethylideneoxanilide.** By HANS VON PECHMANN and OTTO ANSEL (*Ber.*, 1900, 33, 1297—1301. Compare *Abstr.*, 1898, i, 135, and this vol., i, 287).—The final product of the action of acetic anhydride on glyoxime-N-phenyl ether is vinylideneoxanilide. By allowing the acetic anhydride to act for only 3 minutes, the authors have isolated an intermediate product, *hydroxyethylideneoxanilide*, which crystallises in lustrous, white leaflets melting at 174°, gives a yellow coloration with concentrated sulphuric acid, is only with difficulty attacked by oxidising agents, and on further treatment with acetic anhydride and anhydrous sodium acetate, yields vinylideneoxanilide. On treatment with an ethereal solution of diazomethane, it yields *methoxyethylideneoxanilide*, which crystallises in soft, white, matted needles melting at 223—224°, and on hydrolysis yields oxanilide.

In an analogous manner, glyoxime-N-phenyl ether and propionic anhydride yield *hydroxypropylideneoxanilide*, which melts at 160°, gives a yellow coloration with sulphuric acid, and is easily converted into methylvinylideneoxanilide. R. H. P.

**Sulphonic Acids of the Acetylxylidines.** By ALFRED JUNGHAHN (*Ber.*, 1900, 33, 1364—1366).—The sulphonic acids of the acetylxylidines can be obtained in the solid form by direct sulphonation, and the corresponding acids of the acetyltoluidines and of acetylaniline can be prepared in a similar manner. *Acetyl-1:4:2-xylidine-5-sulphonic acid* crystallises with  $2H_2O$  in long, greyish-white needles; on hydrolysis, it yields 1:4:2-xylidine-5-sulphonic acid. *Acetyl-1:3:4-xylidine-6-sulphonic acid* crystallises with  $2H_2O$  in small, white, quadratic prisms or large tablets. The sulphonic acids of acetyltoluidine and acetylaniline will form the subject of a futuro communication.

A. H.

**Phenylcyanamide.** By WILHELM TRAUBE and ERNST VON WEDELSTÄDT (*Ber.*, 1900, 33, 1383—1386. Compare this vol., i, 340).—Phenylmethylecyanamide is readily obtained when phenylcyanamide is treated with sodium ethoxide and methyl iodide. *Phenylbenzylcyanamide* melts at 64°, is insoluble in water, but dissolves readily in

most organic solvents, and, when boiled with dilute hydrochloric acid, yields benzylaniline.

When a considerable excess of ethylene bromide is added to an alcoholic solution of sodium phenyleyanamide, the product is *phenylbromoethyleyanamide*,  $\text{CN}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , which, after recrystallisation from dilute alcohol, melts at  $42^\circ$ ; when, however, an excess of the sodium derivative is used, *dicyanodiphenylethylenediamine*,  $\text{C}_2\text{H}_4(\text{NPh}\cdot\text{CN})_2$ , is formed; this melts at  $133^\circ$ , and when boiled with hydrochloric acid is decomposed, yielding a substance which, on the addition of sodium hydroxide, separates in the form of colourless crystals melting at  $162^\circ$ .

*Ethyl cyanophenyluminoacetate*,  $\text{CN}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , melts at  $49^\circ$ ; chloroacetone and sodium phenyleyanamide give a compound melting at  $130^\circ$ .

J. J. S.

**Action of Certain Acid Reagents on Substituted Carbamides.** By FRANK B. DAINS (*J. Amer. Chem. Soc.*, 1900, 22, 181—198).—By the action of acid chlorides and anhydrides on substituted carbamides, acylcarbamides are probably formed, but, on account of the high temperature required to effect reaction, only their decomposition products can be isolated.

Cain and Cohen (*Trans.*, 1891, 59, 329) have shown that when pure acetic acid and diphenylthiocarbamide are heated at  $130^\circ$ — $140^\circ$  for 3—4 hours, diphenylcarbamide is produced. The author finds that if this mixture is heated on the water-bath for 30 hours, it yields phenylthiocarbimide, acetanilide, and triphenylguanidine, but that if aqueous acetic acid (75 per cent.) is employed, the final products are acetylaniline and diphenylcarbamide. Triphenylguanidine picrate melts at  $180^\circ$ , and not at  $178^\circ$ , as usually stated. When butyric acid is allowed to act on diphenylthiocarbamide at  $140^\circ$ — $160^\circ$ , carbon dioxide and hydrogen sulphide are evolved, and butyrylaniline and diphenylcarbamide obtained. Benzoic acid and salicylic acid react with diphenylthiocarbamide, and benzoic acid with di-*p*-tolylthiocarbamide, in a corresponding manner.

When diphenylthiocarbamide is heated with oxalic acid at  $160^\circ$ — $180^\circ$ , the products are carbon dioxide, hydrogen sulphide, and oxanilide. Succinic acid reacts with diphenylthiocarbamide at  $170^\circ$  with formation of carbon dioxide, hydrogen sulphide, succinyl, and succinylaniline, together with small quantities of aniline and phenylthiocarbimide; a similar decomposition occurs when succinic anhydride is employed, as shown by Dunlap (*Abstr.*, 1896, i, 471). The action of phthalic acid on diphenylthiocarbamide results in the production of hydrogen sulphide, carbon dioxide, phenylthiocarbimide, phthalanil, and a little aniline; phthalic anhydride behaves in a similar manner, as pointed out by Dunlap (*loc. cit.*). When di-*p*-tolylthiocarbamide is heated with phthalic anhydride at  $160^\circ$ , carbon oxysulphide, *p*-tolylthiocarbimide, and *p*-tolylphthalanil are produced.

The acyl derivative, formed by the interaction of an acid chloride and a disubstituted carbamide, appears to break down into an anilide and a carbimide, which further react, giving carbon dioxide and an amidine derivative. When diphenylcarbamide and acetyl chloride are

heated together for 3 hours at  $150^{\circ}$ , carbon dioxide, acetylaniline, and  $\alpha$ -diphenylethenylamidine are produced; the platinichloride of the last-mentioned substance melts at  $210^{\circ}$ , and the picrate at  $165^{\circ}$ .  *$\alpha$ -Diphenylbutenylamidine*,  $C_3H_7 \cdot C(NPh) \cdot NHPh$ , obtained, together with carbon dioxide and butyrylaniline, by the action of butyryl chloride on diphenylcarbamide at  $150$ — $170^{\circ}$ , crystallises from alcohol in needles, melts at  $105^{\circ}$ , and yields a platinichloride. A similar reaction takes place when benzoyl chloride is employed; diphenylbenzamidine picrate melts at  $216^{\circ}$ .

Deninger (Abstr., 1895, i, 461) has shown that, in the presence of pyridine, acid chlorides react with diphenylthiocarbamide at the ordinary temperature with formation of stable substitution products. The author finds that, in the absence of pyridine, heat is required to effect reaction, and no acyl thiocarbamide can be isolated, but a thio-carbimide and an anilide are the principal products, whilst occasionally a small quantity of an amidine base is formed. The action of acetyl, butyryl, and benzoyl chlorides on diphenylthiocarbamide, and the action of benzoyl chloride on di-*m*-xylylthiocarbamide and on di-*o*-tolylthiocarbamide are described. Acetyl chloride reacts with allylphenylthiocarbamide, giving rise to phenylthiocarbimide and *N*-phenylpropylene- $\psi$ -thiocarbamide.

The isocarbamide ethers are readily attacked by organic acids, as the author has previously pointed out (Abstr., 1899, i, 592), whereas the thio-ethers are remarkably stable towards them. By the action of acetic anhydride on amylisodi-*o*-tolylcarbamide at  $150$ — $160^{\circ}$ , amyl acetate, *o*-acetyltoluidine, and a trace of *o*-ditolylcarbamide are formed; under similar conditions, ethylisodiphenylcarbamide yields ethyl acetate and acetylaniline, while methylisodi-*o*-tolylcarbamide furnishes methyl acetate and *o*-acetyltoluidine.

When ethylisodiphenylthiocarbamide is boiled with acetic anhydride, an acetyl additive product,  $NHPh \cdot C(NPhAc)(SEt) \cdot OAc$ , is obtained as a yellow oil, which is soluble in ether, and is decomposed by alcoholic potassium hydroxide with formation of mercaptan and diphenylcarbamide; if, however, the mixture is heated in a sealed tube at  $190^{\circ}$ , mercaptan, ethyl acetate, and acetylaniline are produced. *Acetyl ethylisodiphenylthiocarbamide*,  $NPh \cdot C(NPhAc) \cdot SEt$ , is obtained as a thick oil by the action of acetyl chloride (1 mol.) on a chloroform solution of ethylisodiphenylthiocarbamide (2 mols.) at the ordinary temperature; it is not affected by boiling with glacial acetic acid, but on heating with alcoholic sodium hydroxide, yields sodium acetate, mercaptan, and diphenylthiocarbamide. Benzoyl chloride reacts with ethylisodiphenylthiocarbamide in a similar manner, yielding an oily benzoyl derivative, which is decomposed on heating. E. G.

**Colour of Picric Acid and its Solutions.** By WILHELM MARCKWALD (*Ber.*, 1900, 33, 1128).—Picric acid, when crystallised from concentrated hydrochloric acid, is nearly colourless, but on washing the colourless crystals with water the yellow colour is restored; moreover, the acid mother liquor, which is initially nearly colourless, becomes yellow on strongly diluting. The colour of picric acid thus appears to be due to the coloured ion,  $C_6H_2(NO_2)_3O$ ; when pure

yellow picric acid is dried in a vacuum over sulphuric acid, it becomes colourless owing to the prevention of dissociation within the crystals. A solution of picric acid in light petroleum is nearly colourless, but becomes bright yellow on shaking with water. W. A. D.

**Action of Ethylidene Chloride on Phenols.** By R. FOSSE and J. ETTLINGER (*Compt. rend.*, 1900, 130, 1194—1196).—*Acetal m-cresol*,  $\text{CH}_3\cdot\text{CH}(\text{OC}_6\text{H}_4\text{Me})_2$ , obtained by heating together 1 mol. of ethylidene chloride, 2 mols. of potassium hydroxide, and 2 mols. of *o*-cresol at 120° in a sealed tube, is a colourless, oily liquid boiling at 180—185° under 27 mm. pressure, and at 173—175° under 16 mm. pressure, is insoluble in water or alkalis, but soluble in alcohol, ether, or benzene. When cooled to a low temperature, it solidifies to a white mass which melts at about 12°. When hydrolysed with dilute sulphuric acid, it yields acetaldehyde and *o*-cresol.

*Acetal p-cresol* is a colourless, oily liquid boiling at 200—204° under 22 mm. pressure, which can be solidified to a white mass melting at 15—17°; in other respects, it resembles the ortho-compound. When resorcinol, potassium hydroxide, and ethylidene chloride are heated together in a sealed tube, the compound produced is identical with the acetal resorcinol obtained by Causse from acetaldehyde and resorcinol (*Abstr.*, 1887, 40). H. R. LE S.

**2:6-Diphenyl-4-nitrophenol and 2-Phenyl-4-nitrophenol.** By HENRY B. HILL (*Ber.*, 1900, 33, 1241—1242).—2:6-*Diphenyl-4-nitrophenol*, obtained by the condensation of dibenzyl ketone with nitromalonic aldehyde in alkaline solution (compare Hill and Torrey, *Abstr.*, 1899, i, 788), crystallises from alcohol in colourless prisms and melts at 135—136° (corr.); the corresponding aminophenol, quinone, and quinol, melt respectively at 149—150° (corr.), 135—136° (corr.), and 179—180° (corr.) (compare Borsche, this vol., i, 24).

2-*Phenyl-4-nitrophenol*, obtained similarly from benzyl methyl ketone, crystallises from boiling water or dilute acetic acid in long, yellow needles, and melts at 125—126°; the corresponding aminophenol melts at 198—199° (corr.), and the quinone at 112—113° (corr.) (compare Borsche, *loc. cit.*). W. A. D.

**Preparation of Anthranilic Acid from *o*-Nitrotoluene.** By L. PREUSS and A. BINZ (*Zeit. angew. Chem.*, 1900, 16, 385—386).—Anthranilic acid can be prepared in small yield by fusing *o*-nitrotoluene with powdered sodium or potassium hydroxide. It is readily formed when *o*-nitrotoluene is heated for some hours on the water-bath with concentrated solutions of the alkalis, but dilute solutions produce only a trace. Alcoholic potash is also effective, so that anthranilic acid is produced when *o*- and *p*-nitrotoluenes are separated by Reverdin and La Harpe's method (*Bull. Soc. Chim.*, 1880, [ii], 50, 44). Atmospheric oxygen plays no part in the reaction. R. L. J.

**Formation of Chains.** XLIV. **The Three Sodium Tolyloxides and Ethyl Esters of  $\alpha$ -Bromo-fatty Acids.** By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1249—1261).—*Ethyl  $\alpha$ -o-tolyloxypropionate*,  $\text{C}_7\text{H}_7\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , is a colourless oil of sp. gr. 1.043 at 19°/19°; which boils at 140° under 10 mm., and at 245—246° under 760 mm.

pressure; it is readily hydrolysed by aqueous potassium hydroxide to the *o*-acid, which separates from ether in large crystals, and melts at  $93^{\circ}$ . The *m*-ester is a colourless oil which boils at  $252^{\circ}$  under 743 mm. pressure; the *m*-acid crystallises from a mixture of ether and petroleum in plates and needles, and from benzene in slender needles, dissolves readily in other solvents, melts at  $106\text{--}108^{\circ}$ , and gives a violet coloration when warmed with nitric acid, a property which is also shared by the other *m*-tolxyloxy-acids. The *p*-ester is a colourless oil of density 1.043 at  $19^{\circ}/4^{\circ}$ , which boils at  $150\text{--}151^{\circ}$  under 33 mm. pressure, and at  $255\text{--}256^{\circ}$  under 760 mm. pressure; the *acid* crystallises in long, glistening needles, and melts at  $100\text{--}101^{\circ}$ .

*Ethyl  $\alpha$ -o-tolxyloxybutyrate*,  $C_7H_7 \cdot O \cdot CHEt \cdot CO_2Et$ , is a colourless oil which boils at  $254\text{--}255^{\circ}$ ; the *o*-acid crystallises from light petroleum in colourless needles, dissolves readily in organic solvents, but only slightly in water, and melts at  $49\text{--}52^{\circ}$ . The *m*-ester is a colourless oil which boils at  $262\text{--}263^{\circ}$  under 745 mm. pressure; the *m*-acid crystallises from light petroleum in needles and melts at  $72\text{--}74^{\circ}$ . The *p*-ester boils at  $266.5^{\circ}$  under 743 mm. pressure; the *acid* crystallises from light petroleum in needles and four-sided tablets, and melts at  $63\text{--}65^{\circ}$ .

*Ethyl  $\alpha$ -o-tolxyloxyisobutyrate* is a colourless oil of sp. gr. 1.032 at  $19^{\circ}$ , which boils at  $147^{\circ}$  under 39 mm., and at  $245\text{--}248^{\circ}$  under 760 mm. pressure; the *acid* crystallises in stout, rectangular prisms, and melts at  $75\text{--}76^{\circ}$ . The *m*-ester is a colourless oil, and boils at  $253^{\circ}$  under 745 mm. pressure; the *m*-acid crystallises from light petroleum in square tablets, and melts at  $66.5\text{--}67.5^{\circ}$ . The *p*-ester is a colourless oil of sp. gr. 1.032 at  $19^{\circ}$ , boils at  $150^{\circ}$  under 39 mm. pressure, and at  $254\text{--}258^{\circ}$  under 760 mm. pressure; the *p*-acid crystallises from light petroleum in large six- and eight-sided tablets, and melts at  $71\text{--}72^{\circ}$ .

*Ethyl o-tolxyloxyisovalerate*,  $C_7H_7 \cdot O \cdot CHPr^{\beta} \cdot CO_2Et$ , is a colourless oil which boils at  $258\text{--}261^{\circ}$ ; the *acid* crystallises from light petroleum in soft, slender needles, and melts at  $86\text{--}87^{\circ}$ . The *m*-ester is a colourless oil which boils at  $265\text{--}266^{\circ}$  under 745 mm. pressure; the *m*-acid crystallises from light petroleum in colourless prisms, and melts at  $61\text{--}63.5^{\circ}$ . The *p*-ester boils at  $145\text{--}148^{\circ}$  under 55 mm. pressure, and at  $265\text{--}271^{\circ}$  under 760 mm. pressure; the *p*-acid crystallises from light petroleum in colourless, four-sided tablets, and melts at  $81\text{--}82^{\circ}$ .  
T. M. L.

**Formation of Chains. XLV. Sodium Xylyloxides and Ethyl Esters of  $\alpha$ -Bromo-fatty Acids.** By CARL A. BISCHOFF (*Ber.*, 1900, 1261—1269).—*Ethyl  $\alpha$ -o-xylyloxypropionate*,

$C_6H_3Me_2 \cdot O \cdot CHMe \cdot CO_2Et$  [Me : Me : OR = 1 : 2 : 4], is a yellowish oil which boils at  $268\text{--}273^{\circ}$  under 773 mm. pressure; the *o*-acid crystallises from a mixture of ether and light petroleum in square rods and plates, and melts at  $85\text{--}88^{\circ}$ . The *m*-ester [Me : Me : OR = 1 : 3 : 4] boils at  $264.5^{\circ}$  under 771 mm. pressure; the *m*-acid crystallises from a mixture of ether and light petroleum in colourless prisms, and melts at  $82\text{--}87.5^{\circ}$ . The *p*-ester [Me : Me : OR = 1 : 4 : 5] is a colourless oil which boils at  $259^{\circ}$  under 782 mm. pressure; the *p*-acid crystallises from light petroleum in four-sided prisms and tablets, and melts at  $105\text{--}106.5^{\circ}$ .

*Ethyl α-o-xylyloxybutyrate* is a yellowish oil and boils at 275—280° under 773 mm. pressure. The *o-acid* crystallises from light petroleum in colourless needles, and melts at 73—76°. The *m-ester* is a colourless oil which boils at 267—271° under 769 mm. pressure. The *m-acid* crystallises from a mixture of ether and light petroleum in soft, colourless needles, and melts at 64·3—65·3°. The *p-ester* boils at 265—266° under 765 mm. pressure. The *p-acid* crystallises from a mixture of ether and light petroleum in soft, colourless needles, and melts at 87—90°.

*Ethyl α-o-xylyloxyisobutyrate* is a yellowish oil of characteristic odour, and boils at 263—268° under 774 mm. pressure; the *acid* crystallises from light petroleum in yellowish plates, and melts at 86—90·5°. The *m-ester* boils at 255—258° under 769 mm. pressure. The *m-acid* was obtained as a yellow oil. The *p-ester* is a colourless oil which boils at 265—266° under 767 mm. pressure. The *p-acid* crystallises from a mixture of ether and light petroleum in four-sided tablets and melts at 114°.

*Ethyl α-o-xylyloxyisovalerate* is a colourless oil which boils at 275—283° under 744 mm. pressure. The *o-acid* crystallises from light petroleum in prisms, and melts at 49·5—52°. The *m-ester* is a colourless oil which boils at 267—274° under 769 mm. pressure; the *m-acid* is a yellowish oil which boils at 213° under 42 mm. pressure. The *p-ester* is a colourless oil which boils at 270° under 769 mm. pressure. On hydrolysis, it gives crystals of *p*-xylenol in addition to the *p-acid* which was obtained as a yellow oil. T. M. L.

Formation of Chains. XLVI. Sodium Derivatives of Carvacrol, Thymol, and *ψ*-Cumenol with Ethyl Esters of *α*-Bromofatty Acids. By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1269—1277).—*Ethyl α-carvacroxypropionate*,  $C_6H_3MePr \cdot O \cdot CHMe \cdot CO_2Et$  [Me : Pr : OR = 1 : 4 : 6], is a colourless oil which boils at 277—279° under 751 mm. pressure; the *acid* separates from light petroleum in colourless crystals and melts at 81·5—82·5°.

*Ethyl α-carvacroxybutyrate* boils at 283—286° under 751 mm. pressure; the *acid* boils at 224—225° under 59 mm. pressure, and solidifies to crystals which melt at 42·5—43·5°.

*Ethyl α-carvacroxyisobutyrate* boils at 262—272° under 751 mm. pressure, the *acid* at 190—200° under 93 mm. pressure.

*Ethyl α-carvacroxyisovalerate* boils at 280—292° under 762 mm. pressure, the *acid* at 226—229° under 68 mm. pressure.

*Ethyl α-thymoxypropionate* [Me : Pr : OR = 1 : 4 : 5] boils at 267—272° under 760 mm. pressure; the *acid* crystallises from a mixture of ether and light petroleum in large, colourless tablets, and melts at 68·5—69°.

*Ethyl α-thymoxybutyrate* boils at 273—278° under 773 mm. pressure; the *acid* crystallises from a mixture of ether and light petroleum in large, triclinic prisms, and melts at 74—76·5°.

*Ethyl α-thymoxyisobutyrate* boils at 258—263° under 760 mm. pressure; the *acid* crystallises from light petroleum in minute needles and melts at 69—71°.

*Ethyl α-thymoxyvalerate* boils at 275—283° under 760 mm. pressure, and the *acid* boils at 228—229° under 60 mm. pressure.

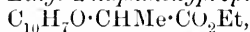


*Ethyl  $\alpha$ -cumenoxypropionate*,

$C_6H_5Me_3O \cdot CHMe \cdot CO_2Et$  [ $Me : Me : OH : Me = 1 : 2 : 4 : 5$ ],  
boils at  $147-149^\circ$  under 20 mm. pressure; the *acid* crystallises from alcohol in colourless tablets and melts at  $147^\circ$ . T. M. L.

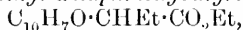
**Formation of Chains. XLVII. Sodium Naphthyloxides and Ethyl Esters of  $\alpha$ -Bromo-fatty Acids.** By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1386—1392).—The sodium derivatives of  $\alpha$ - and  $\beta$ -naphthol (compare Schäffer, *Annalen*, 1869, 152, 286) may readily be obtained in a pure state by treating the naphthols with the theoretical amount of sodium ethoxide dissolved in alcohol and subsequent heating under reduced pressure until the weight is constant. These sodium derivatives have been respectively heated for 4 hours at  $160^\circ$  with the ethyl esters of  $\alpha$ -bromopropionic,  $\alpha$ -bromobutyric,  $\alpha$ -bromoisobutyric, and  $\alpha$ -bromoisovaleric acids, and the resulting products fractionated first under ordinary and, finally, under reduced pressure.

[With KISLIANSKY.]—*Ethyl  $\alpha$ -naphthoxypropionate*,



is a pale yellow oil, distilling at  $195^\circ$  under 8 mm., or at  $205^\circ$  under 22 mm. pressure. The *acid* crystallises from benzene in minute, colourless plates melting at  $153^\circ$ , and is only sparingly soluble in hot water, cold benzene, or light petroleum.

[With LIPSCHITZ.]—*Ethyl  $\alpha$ -naphthoxybutyrate*,



distils at  $190-194^\circ$  under 5 mm. pressure, and has a specific gravity 1.102 at  $18.6^\circ/4^\circ$ . The *acid* crystallises in colourless needles and melts at  $113-114^\circ$ . *Ethyl  $\alpha$ -naphthoxyisobutyrate*,  $C_{10}H_7O \cdot CMe_2 \cdot CO_2Et$ , distils at  $190-193^\circ$  under 6 mm. pressure, and the *acid* melts at  $130-131^\circ$ . *Ethyl  $\alpha$ -naphthoxyisovalerate* distils at  $208^\circ$  under 10 mm. pressure, and the corresponding *acid* melts at  $89.5-90.5^\circ$ .

[With SLOBODSKOI.]—*Ethyl  $\beta$ -naphthoxypropionate* crystallises from alcohol in rhombic prisms. The *acid* crystallises in mono- or tri-clinic plates melting at  $107-108^\circ$ .

[With COX.]—*Ethyl  $\beta$ -naphthoxybutyrate* is a pale yellow oil distilling at  $200-203^\circ$  under 12 mm. pressure. The *acid* crystallises from water in needles melting at  $126.5^\circ$ .

[With SIW.]—*Ethyl  $\beta$ -naphthoxyisobutyrate* distils at  $195-200^\circ$  under 6 mm. pressure, and the *acid* crystallises in prismatic plates melting at  $123^\circ$ .

[With DOWGALLO.]—*Ethyl  $\beta$ -naphthoxyisovalerate* boils at  $212^\circ$  under 13 mm. pressure, and the *acid* crystallises in needles melting at  $110^\circ$ .

Quantitative experiments have been made by boiling the two sodium derivatives (1 mol.) with solutions of the bromo-esters (2 mols.) in light petroleum (b. p.  $65-70^\circ$ ) for 1 hour. The following results show the percentage of the sodium derivative that has entered into reaction :

	$\alpha$ -Naphthol.		$\beta$ -Naphthol.	
$\alpha$ -Bromopropionate .....	81.0	82.5	91.0	91.5
$\alpha$ -Bromobutyrate .....	84.5	85.0	84.0	88.0
$\alpha$ -Bromoisobutyrate .....	15.0	20.5	37.0	39.0
$\alpha$ -Bromoisovalerate .....	11.0	9.5	21.0	21.5

J. J. S.

**Formation of Chains. XLVIII. Guaiacol Derivatives.** By CARL A. BISCHOFF (*Ber.*, 1900, **33**, 1392—1397).—The sodium derivative of guaiacol is readily obtained by treating guaiacol with an alcoholic solution of sodium ethoxide and heating the residue to 120° under reduced pressure. This sodium derivative has been treated with the ethyl esters of the  $\alpha$ -bromo-fatty acids mentioned in the preceding abstract.

*Ethyl  $\alpha$ -guaiacoxypropionate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , is a colourless liquid with a strong, alliaceous odour, and distils at 272—277° under 740 mm. pressure. The *acid* melts at 85° and dissolves in most organic solvents; with hydrochloric acid, it gives a reddish-yellow colour, and with warm nitric acid a bordeaux red. When the acid is heated with phenetidine for 8 hours at 160°, it yields *guaiacoxypropionylphenetidine*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , which crystallises from alcohol in colourless needles melting at 96.5°. It is non-poisonous, and may be employed in cases of influenza. The same compound may be more readily prepared by the action of the sodium derivative of guaiacol on an alcoholic solution of  *$\alpha$ -bromopropionylphenetidine* (melting at 135°). Bromoacetylphenetidine melts at 171.5—176°, and reacts with an alcoholic solution of sodium guaiacol, yielding Lederer's guaiacoxylacetylphenetidine, melting at 103°.

*Ethyl  $\alpha$ -guaiacoxybutyrate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , distils at 274—276° under 744 mm. pressure, and has an odour similar to that of butyric acid. The *acid* crystallises in needles melting at 75—76°. *Ethyl  $\alpha$ -guaiacoxylisobutyrate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , distils at 272—273° under atmospheric pressure, and the *acid* is an oil. *Ethyl  $\alpha$ -guaiacoxylisovalerate* distils at 275—285° at 751 mm. pressure, and yields an *acid* melting at 98—98.5°.

*Ethyl guaiacoxymalonnate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , distils at 205° under 13 mm. pressure, and when hydrolysed yields the corresponding acid, which reacts with phenetidine.

The following numbers give the percentage of the sodium derivative which enters into reaction when heated in light petroleum (b. p. 65—70°) solution for 1 hour with the different esters:

Ethyl $\alpha$ -bromopropionate .....	39.5	40.0
Ethyl $\alpha$ -bromobutyrate .....	28.0	28.5
Ethyl $\alpha$ -bromoisobutyrate .....	3.2	3.5
Ethyl $\alpha$ -bromoisovalerate .....	2.5	3.5

From these results, it appears that guaiacol lends itself less readily to chain formation than any of the phenols hitherto investigated.

J. J. S.

**Formation of Chains. XLIX. Derivatives of the three Ethyl Hydroxybenzoates.** By CARL A. BISCHOFF [with, in part, BELAKOWSKI, GUNTUM, KOCH, KRUSENSTIERN, MERGENTHALER, ROTHAL, and RZUCHOWSKI] (*Ber.*, 1900, **33**, 1398—1407. Compare ROSSING, *Abstr.*, 1885, 388; AUWERS and HAYMANN, *ibid.*, 1895, i, 44).—The sodium derivatives of ethyl *o*-, *m*-, and *p*-hydroxybenzoates (1 mol.) have been heated with the ethyl esters of  $\alpha$ -bromo-fatty acids (2 mols.) for 4 hours at 160° and the products investigated.

*Ethyl α-salicyloxypropionate*,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , distils at  $214\text{--}215^\circ$  under 55 mm. pressure, and on hydrolysis yields the corresponding *acid* melting at  $137\text{--}139^\circ$ . The bye-products which are formed in the preparation of the ester have not been obtained in a pure state.

*Ethyl α-salicyloxybutyrate* distils at  $199\text{--}201^\circ$  under 17 mm. pressure, and the *acid* crystallises in colourless plates melting at  $130^\circ$ . *Ethyl α-salicyloxyisobutyrate* distils at  $193^\circ$  under 21 mm. pressure, and the corresponding *acid* crystallises in needles melting at  $108\text{--}109^\circ$ . *Ethyl salicyloxyisovalerate* distils at  $185\text{--}190^\circ$  under 4 mm. pressure, and the corresponding *acid* melts at  $129\text{--}130^\circ$ . In the preparation of the ester, a considerable amount of *ethyl isopropylketocoumarancarboxylate*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CPr}^\beta \cdot \text{CO}_2\text{Et}$ , is always formed; it crystallises in long, colourless needles melting at  $77\text{--}78^\circ$ .

The following numbers give the percentage amounts of the sodium derivatives entering into reaction when boiled with the ethyl esters (2 mols.) for 1 hour in light petroleum (b. p.  $65\text{--}70^\circ$ ):

	<i>Ortho.</i>		<i>Meta.</i>		<i>Para.</i>	
Ethyl α-bromopropionate...	21.55	23.05	28.0	29.8	13.25	16.0
„ α-bromobutyrate ...	8.25	9.1	12.0	13.3	11.75	12.5
„ α-bromoisobutyrate...	1.8	2.5	2.55	2.9	1.5	3.54
„ α-bromoisovalerate...	0.6	0.6	2.85	3.14	2.0	3.0

It thus appears that sodium derivatives of the ester of hydroxybenzoic acids condense less readily even than the sodium derivative of guaiacol.

*Ethyl hydrogen p-carboxyphenoxypionate*,

$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$  or  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , crystallises in colourless needles melting at  $103^\circ$ ; the normal *ethyl* ester is a thick, colourless oil distilling at  $210\text{--}215^\circ$  under 20 mm. pressure, and the *acid* crystallises in colourless needles melting at  $211\text{--}212^\circ$ .

The sodium derivatives of the *o*- and *m*-hydroxy-esters were obtained by Freer's method (Abstr., 1893, i, 66), and that of the *para*-compound by the action of alcoholic sodium ethoxide on the ester and subsequent heating in a vacuum. J. J. S.

**Isomeric Phenylparaconic Acids.** By RUDOLPH FITTIG (*Ber.*, 1900, 33, 1294—1295. Compare Abstr., 1899, i, 437).—It has been shown that phenylitaconic acid is regenerated from phenylitaconic acid by the action of bromine in sunlight; in diffused light, however, a phenylbromoparaconic acid is formed, which, on reduction with sodium amalgam, yields an isomeride of phenylparaconic acid; this *isophenylparaconic acid* melts at  $168^\circ$ . Phenylparaconic acid is a racemic compound, and has been separated into its active components by means of the strychnine salts. R. H. P.

**Acetylphenylacetylene and Benzoylphenylacetylene.** By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1900, 130, 1259—1261. Compare Nef, this vol., i, 20).—An aqueous solution of potassium hydroxide has no action on acetylphenylacetylene or benzoylphenylacetylene in the cold, but when boiling it hydrolyses the former into phenylacetylene and acetic acid, and the latter into benzoic acid

and acetophenone. Alcoholic potash yields the same compounds with benzoylphenylacetylene, whereas acetylphenylacetone is decomposed into tarry products. G. T. M

**A Dihydrodisulphonic Acid derived from Carvone.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1900, [iii], 23, 280—286).—Carvone does not yield a normal compound with sodium hydrogen sulphite, but when boiled for about an hour in a reflux apparatus with a solution of sodium hydrogen sulphite and sodium carbonate, it is completely dissolved with the formation of *sodium carvonedihydrodisulphonate*,  $C_{10}H_{16}O_7S_2Na_2$ . This compound, which was obtained as a deliquescent, white, or yellowish-white, powder, is not decomposed by alkalis and forms a *semicarbazone*, thus showing that the fixation of the sodium hydrogen sulphite is effected only by the ethylene linkings, the carbonyl group remaining unaltered.

The formation of this substance affords a means for the accurate estimation of carvone in essential oils, the oil unattacked by the sodium hydrogen sulphite solution being subsequently weighed and the carvone obtained by difference, or the sulphite utilised in the formation of the compound determined by titration with potassium iodide solution before and after the experiment. Limonene, which usually accompanies carvone in essential oils, also forms a dihydrodisulphonate derivative, an amorphous, white powder of the composition  $C_{10}H_{16}(SO_3HNa)_2$ ; this is, however, formed with such difficulty, a yield of only 2 per cent. being obtained after 18 hours boiling with the sodium hydrogen sulphite solution, that the estimation of carvone by the process described is not appreciably affected thereby. N. L.

**isoFenchyl Alcohol.** By JULIUS BERTRAM and J. HELLE (*J. pr. Chem.*, 1900, [ii], 61, 293—306).—Fenchyl alcohol is best purified by conversion into, and subsequent hydrolysis of, *fenchyl hydrogen phthalate*, which crystallises from alcohol and melts at  $145-145.5^\circ$ . *Fenchyl formate* boils at  $115^\circ$  under 40 mm., and at  $84-85^\circ$  under 13 mm. pressure, has a sp. gr. 0.988 at  $15^\circ$ , and a rotation  $\alpha_D -73.14'$ ; *fenchyl acetate* boils at  $87-88^\circ$  under 10 mm. pressure, has a sp. gr. 0.9748 at  $15^\circ$ , and a specific rotation  $[\alpha]_D -58.08^\circ$ . *Fenchyl phenylurethane* forms broad needles or tablets melting at  $82-82.5^\circ$ .

The fenchene prepared by the authors according to Wallach's method (Abstr., 1891, 1088), using, however, quinoline instead of aniline, boiled at  $154-156^\circ$ , had a sp. gr. 0.8660—0.8665 at  $15^\circ$ , and a refractive index  $[n]_D 1.46733-1.46832$  at  $17^\circ$ .

*isoFenchyl alcohol*, prepared from fenchene in a similar manner to the preparation of *isoborneol* from camphene (Bertram and Walbaum, Abstr., 1894, i, 204), crystallises in colourless, flexible needles, melts at  $61.5-62^\circ$ , boils at  $97-98^\circ$  under 13 mm. pressure, has a sp. gr. 0.9613 at  $15^\circ$ , a refractive index  $[n]_D 1.48005$  at  $15^\circ$ , and a specific rotation in alcoholic solution  $[\alpha]_D -25.73^\circ$ . It is a saturated secondary alcohol and forms an *acetate*, which boils at  $98-99^\circ$  under 14 mm. pressure, and has a sp. gr. 0.974 at  $15^\circ$ . The acetate obtained from fenchene and glacial acetic acid boils at  $89-90^\circ$  under 8 mm. pressure, and has a sp. gr. 0.9724 at  $15^\circ$ . *isoFenchyl hydrogen phthalate*, prepared for the purification of the alcohol, is a colourless, crystalline powder,

melting at 149—150°. *isoFenchyl phenylurethane* crystallises from alcohol and melts at 106—107°. When treated with zinc chloride in benzene solution, *isofenchyl* alcohol yields a hydrocarbon, which is probably identical with fenchene. On oxidation with chromic acid, it yields a *ketone*,  $C_{10}H_{16}O$ , which boils at 193—194°, has a sp. gr. 0.950 at 15°, and a refractive index  $[n]_D$  1.46189, and forms an *oxime*, which crystallises in compact prisms melting at 82°; on reduction with sodium and alcohol, it yields an *alcohol*, which boils at 83—84° under 8 mm. pressure, and yields a *hydrogen phthalate*, which melts at 110—111°.

R. H. P.

**Camphane.** By OSSIAN ASCHAN (*Ber.*, 1900, 33, 1006—1010).—In order to decide whether camphor yields an active or inactive camphane,  $C_{10}H_{18}$ , and thus to confirm one or other of the various formulæ which have been proposed for camphor, pinene hydriodide, which has been shown by Wagner and Brickner (this vol., i, 46) to be a true ether of borneol, was submitted to reduction. This is best carried out in acetic acid solution by means of zinc and hydriodic acid, when a perfectly inactive camphane is obtained, which crystallises in six sided plates, and melts at 153—154°. The pinene hydriodide employed was only very faintly active, and it is possible that this was due to the presence of a small amount of an active impurity.

A. H.

**The Rendering Active of Oxygen.** IV., V., and VI. By CARL ENGLER [and in part J. WEISSBERG] (*Ber.*, 1900, 33, 1090—1096, 1097—1109, 1109—1111. Compare *Abstr.*, 1897, ii, 402; 1899, i, 189, 221).—IV. *Autoxidation of oil of turpentine and of some other unsaturated compounds.*—When pure pinene is shaken with a measured quantity of  $N/100$  sodium indigotindisulphonate in a flask containing air until decolorisation of the indigotin has been effected, it is found that the diminution in volume of the air corresponds approximately to twice the oxygen taken up by the indigotin; moreover, the diminution represents 4—5 atoms of oxygen for each molecule of pinene. This bears out the author's view that in such oxidations the oxygen gas is taken up by molecules at a time, peroxides being formed, which give up half their oxygen to substances capable of taking it—"acceptors," whilst the other half oxidises the substance that originally had absorbed the oxygen. Amylene, trimethylene-ethylene and hexylene absorb oxygen in a similar manner; when distilled, the products leave a residue which contains about two atoms of oxygen per mol. of the hydrocarbon.

V. *The phenomena of autoxidation* [with J. WEISSBERG].—Various cases of spontaneous oxidation in the presence of oxygen gas are considered from the authors' point of view (compare especially *Abstr.*, 1897, ii, 402, and above). They are regarded as conditioned by the unsaturated nature of the autoxidiser, or by the presence of labile hydrogen atoms in it, and the following categories are distinguished. (1) The oxygen adds itself on to unsaturated substances and forms peroxides (triethylphosphine, oil of turpentine, hexylene, &c.). (2) The oxygen unites with hydrogen, held in labile combination by the

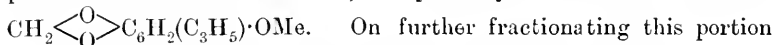
autoxidiser, to form hydrogen peroxide; the remainder of the autoxidiser at once takes up another molecule of oxygen to form a peroxide (benzaldehyde, and probably palladium hydride). (3) The oxygen combines with labile hydrogen of the autoxidiser to form hydrogen peroxide; the remainder is not oxidisable, and either remains as it is, or suffers condensation; it may be a peroxide (hydroxides of alkalis and alkaline earths) or not (hydroxylamines, phenols, azo-compounds).

VI. *Demonstration of the formation of hydrogen peroxide and of other peroxides as products of direct oxidation.*—If a fine jet of burning hydrogen gas is directed against a small block of ice so as to bore a hole into the latter, hydrogen peroxide can be detected in the melted water by adding starch solution, potassium iodide, acid, and a trace of ferrous sulphate, or by shaking with ether and chromic acid; the hydrogen peroxide is cooled by the ice as soon as formed, and so protected from decomposition by the heat of the flame. To show that the peroxide does not result from decomposition of the water by the heat of the flame, a platinum wire rendered incandescent by an electric current is kept for several hours just at the surface of the water; no peroxide can then be detected in the latter. It can also be shown that hydrogen peroxide is formed when carbon monoxide, illuminating gas, alcohol, ether, carbon disulphide, &c., are burned in the same manner.

If sodium is burned on aluminium foil, and the product dissolved in water, hydrogen peroxide is found to be present. A peroxide is also formed when a very narrow, thin strip of magnesium ribbon is burned, or when a stouter piece is burned and held against ice or cold water.

C. F. B.

**Parsley Oil.** By CARLO BIGNAMI and GIUSEPPE TESTONI (*Gazzetta*, 1900, 30, i, 240—253).—The leaves and seeds of *Apium petroselinum* contain, besides apiol and the glucoside apiin, a dense, pale greenish-yellow oil, which boils at 277—285° under ordinary pressure, and has a sp. gr. 1.1206 at 17°. When fractionally distilled, the greater portion boils at 279—285°; it probably has the constitution



On further fractionating this portion and determining the methoxy-groups in the different fractions, varying numbers were obtained. When oxidised with aqueous permanganate, the oil yields as principal product an acid identical with Roser's methylenemethylgallic acid (Abstr., 1890, 528) and with Semmler's myristicin acid (Abstr., 1892, 311). Apiolic acid, trimethylgallic or methylsyringic acid, and a new *tetramethylapionol-carboxylic acid*,  $\text{C}_{11}\text{H}_{14}\text{O}_6$ , are also formed. The latter acid, which separates from light petroleum in stellate groups of large, white, acicular crystals melting at 87°, is readily soluble in benzene, acetone, ethyl acetate, methyl or ethyl alcohol, or boiling water. Its *silver* and *barium* (with  $2\text{H}_2\text{O}$ ) salts are described. On heating with soda lime, the acid loses carbon dioxide, tetramethylapional being formed.

On brominating the original oil in acetic acid solution, an oily product and two isomeric *bromo-derivatives* of the composition

$C_{11}H_{10}O_3Br_4$ , probably  $CH_2 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} C_6Br_2(OMe) \cdot CHBr \cdot CHMeBr$ , are obtained. The first of these crystallises from alcohol in slender, silky needles melting at  $131-134^\circ$ , and is soluble in ethyl acetate; the *iso*-compound separates from alcohol in large, colourless crystals melting at  $162^\circ$ . T. H. P.

**Constituents of West Indian Sandalwood Oil.** By HUGO VON SODEN (*Chem. Centr.*, 1900, i, 858; from *Pharm. Zeit.*, 45, 229. Compare Abstr., 1899, i, 924).—By hydrolysing West Indian sandalwood oil from *Amyris balsamifera* with alcoholic potash, and fractionally distilling in a vacuum, a sesquiterpene alcohol, *amyrol*,  $C_{15}H_{25} \cdot OH$ , is obtained; it is an almost colourless liquid, of about the consistency of Venetian turpentine, has a faint aromatic odour and a bitter taste, boils at  $299-301^\circ$  under 748 mm. and at  $151-152^\circ$  under 11 mm. pressure, dissolves in  $3-3\frac{1}{2}$  parts of 70 per cent. alcohol, and has a sp. gr.  $0.980-0.982$  at  $15^\circ$ , and a rotatory power of about  $+27^\circ$  (100 mm. tube). When heated with phthalic anhydride at  $110^\circ$ , it does not form an ester, but partially decomposes, losing water, and yielding a sesquiterpene. According to Dulière (*J. Pharm.*, 1898, [vi], 7, 553), West Indian sandalwood oil contains 42 per cent. of alcoholic constituents reckoned as santalol, but this result is low, for by the action of acetic anhydride only about 65 per cent. of the alcohol is converted into acetate, the rest forming a sesquiterpene. Amyrol, like santalol, may really consist of two similar alcohols of different rotatory power.

The oil also contains considerable quantities of sesquiterpenes, together with small quantities of substances which have strong odours. The former may be separated from the alcohols of higher boiling point by distilling the hydrolysed oil in a vacuum. E. W. W.

**Santalenes and Santalols.** By M. GUERBET (*Compt. rend.*, 1900, 130, 1324-1327. Compare this vol., i, 242).—When heated in sealed tubes with glacial acetic acid at  $180-190^\circ$ ,  $\alpha$ - and  $\beta$ -santalenes combine very slowly to form the *acetates* of santalene,  $C_{15}H_{23} \cdot C_2H_4O_2$ . The acetate of  $\alpha$ -santalene boils at  $164-165^\circ$ , and the  $\beta$ -compound at  $167-168^\circ$ , the pressure in each case being 14 mm.

The *hydrochlorides*,  $C_{15}H_{23} \cdot 2HCl$ , are prepared by passing hydrogen chloride into a dry ethereal solution of the santalene; they are decomposed on distillation, even in a vacuum. The specific rotation of the  $\alpha$ -compound is  $+6^\circ$ , whilst that of the  $\beta$ -compound is  $+8^\circ$ .

$\alpha$ -Santalene only yields one *nitrosochloride* when treated with nitrosyl chloride; this derivative crystallises from benzene in short prisms, and melts and decomposes at  $122^\circ$ . *a*-Santalene *nitrolepiperidine*, obtained by treating the nitrosochloride with a solution of piperidine in benzene, is readily soluble in alcohol, and crystallises in needles melting at  $108-109^\circ$ .

Two *nitrosochlorides* are produced from  $\beta$ -santalene; these are separated from each other by fractional crystallisation from alcohol; the less soluble melts at  $152^\circ$ , and the other, which forms the main product of the reaction, melts at  $106^\circ$ ; the corresponding *nitroamines* melt at  $101^\circ$  and  $104-105^\circ$  respectively.





yields succinic acid, in addition to volatile acids and a little oxalic acid, when it is oxidised with permanganate in the cold. When sabinol is heated with 10 per cent. alcoholic hydrochloric acid for a little while, *p*-cymene is formed as the chief product. These reactions lead to the adoption of the formulæ given above. C. F. B.

**Indigo Fermentation.** By MARTINUS BEJERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 495—512. Compare this vol., i, 230).—The expression “indigo fermentation” includes two distinct processes, one a katabolic change brought about by the direct action of living protoplasm, the other a decomposition induced by enzymes; in either case, this action can only take place in indigo plants; there can be no fermentation in woad (*Isatis tinctoria*), a plant which contains free indoxyl, but no indigo yielding glucoside.

The preparation of indican and indigo enzyme from *Polygonum tinctorium* and *Indigofera leptostachya* is described in detail. These substances accumulate more particularly in the leaves, and to a less extent in the flowers; they are, however, absent from the roots, stems, and reproductive cells. Microchemical examination of the leaves of *Phajus grandiflorus* showed that the indican is present in the protoplasm, but not in the sap nuclei and cell-walls; the chlorophyll granules contain indigo enzyme, but no glucoside. Indigo enzymes are very seldom found elsewhere than in the indigo plants, but indican is decomposed by emulsin from almonds; glucase from maize, although resembling this enzyme in its action on amygdalin, does not hydrolyse indican. It is found that the indigo enzymes from *Indigofera*, emulsin, *Phajus*, *Saccharomyces sphaericus*, and *Polygonum* are specifically different, having respectively the following temperature optima, 61°, 55°, 53°, 44°, and 42°.

In *Indigofera*, the fermentation is entirely due to enzymes; in *Polygonum* and *Phajus* the action is partly katabolic.

When indican is hydrolysed by bacteria, the action is katabolic, hence the dead organisms have no action on the glucoside.

G. T. M.

**Indican and its Enzyme.** By J. J. HAZEWINCKEL (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 512—520. Compare preceding abstract).—When the leaves of *Indigofera leptostachya* are extracted with boiling water or dilute solutions of calcium hydroxide or mercuric chloride, a solution is obtained which contains an indigo yielding glucoside. The production of indigotin may be brought about by the action of (1) oxidising agents in acid solutions, (2) enzymes derived from the indigo plant or other sources, (3) bacteria. The enzyme from *Indigofera* was obtained by extracting the leaves with concentrated alcohol, drying the residue at the ordinary temperature, and employing it in the form of powder; the active principle contained in the preparation is somewhat soluble in water, but more so in 10 per cent. brine solution.

The glucoside contained in the aqueous extract was not isolated, but it appears to have some properties in common with indican. Indoxyl is formed as an intermediate product in the formation of indigo, confirmatory proof of its presence being obtained by the production of

the indogenides of isatin, benzaldehyde, and pyruvic acid. The presence of indoxyl in the products of hydrolysis accounts for the large amount of indigo-red which is formed in some processes of indigo manufacture.

G. T. M.

**Indican.** By SEBASTIAAN HOOGEWERFF and H. TER MEULEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 520—525. Compare preceding abstracts).—Indican may be obtained from indigo leaves in colourless, spear-shaped crystals by treating an aqueous decoction with barium hydroxide, filtering off impurities, removing excess of the base with carbon dioxide, evaporating the filtrate to dryness, extracting the crude residue with methyl alcohol, adding ether to the extract to precipitate the last traces of foreign substances, distilling off these solvents, dissolving the final residue in water, and allowing the solution to deposit the glucoside. It crystallises with  $3\text{H}_2\text{O}$ , melts at  $51^\circ$ , and passes into a gummy mass at  $100^\circ$ . When dried in a vacuum over sulphuric acid, indican loses its water of crystallisation, and then melts at  $100\text{--}102^\circ$ . Ultimate analysis and cryoscopic molecular weight determinations point to the formula  $\text{C}_{14}\text{H}_{17}\text{NO}_6$ , thus confirming Marchlewski and Radcliffe's hypothesis (*Abstr.*, 1899, i, 387). The glucoside is moderately soluble in water, acetone, or the alcohols, and has a bitter taste; a 2 per cent. solution in a 20 cm. tube at  $15^\circ$  gives a rotation of  $-2^\circ$ ; after hydrolysis and the formation of indigotin, the liquid becomes dextrorotatory. When air is passed through a solution of indican in dilute hydrochloric acid containing a little ferric chloride, 91 per cent. of the glucoside is converted into indigotin, according to the following equation,  $2\text{C}_{14}\text{H}_{17}\text{NO}_6 + \text{O}_2 = \text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2 + 2\text{C}_6\text{H}_{12}\text{O}_6$ , a certain amount of indigo-red being simultaneously produced.

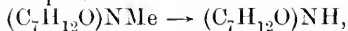
The indican from *Indigofera leptostachya* appeared to be identical with that from *Polygonum tinctorium*.

G. T. M.

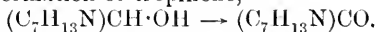
**Chemistry of Chlorophyll: Phyllorubin.** By LEO MARCHLEWSKI (*J. pr. Chem.*, 1900, [ii], 61, 289—292).—When phyllocyanin (*Abstr.*, 1894, i, 341) is heated with alcoholic potash until the alcohol is nearly all evaporated, a viscous, green mass is obtained; this is dissolved in water, acidified and extracted with ether, when the ethereal solution yields an amorphous substance, *phyllorubin*, which shows a spectrum different from that given by phylloporphyrin (*Abstr.*, 1895, i, 297) or phyllotaonin (*Abstr.*, 1896, i, 181).

R. H. P.

**Action of Potassium Permanganate on Bases.** By RICHARD WILLSTÄTTER (*Ber.*, 1900, 33, 1167—1170).—Whilst potassium permanganate oxidises tropine in alkaline solution to tropinenin,



in acid solution, the basic group is protected and the  $\cdot\text{CH}(\text{OH})\cdot$  group is attacked with formation of tropinone,



Lead dioxide in sulphuric acid behaves similarly.

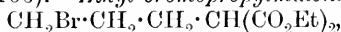
T. M. L.

**Reduction of Tropinone to Tropine and Tropane.** By RICHARD WILLSTÄTTER and FRITZ IGLAUER (*Ber.*, 1900, 33, 1170—1176).—Tropine and  $\psi$ -tropine can be readily separated by means of their

picrates. Tropine picrate crystallises in long trapezoid forms or striated, six-sided tablets, darkens at  $270^{\circ}$ , and decomposes at  $275^{\circ}$  without melting; 0.462 part dissolves in 100 parts of water at  $16^{\circ}$ ;  $\psi$  tropine picrate crystallises in long, pointed needles, begins to decompose at  $245^{\circ}$ , and melts at  $258-259^{\circ}$ ; 1.484 parts dissolve in 100 parts of water at  $14^{\circ}$ .

By reducing tropinone with zinc dust and hydriodic acid at  $0^{\circ}$ , it is converted into a mixture of tropine and  $\psi$ -tropine, together with a smaller amount of tropane; the conversion of the  $\psi$ -tropine, stable towards alkali, into the labile tropine can thus be readily effected by oxidising to tropinone and then reducing. If the reduction is carried out at  $50^{\circ}$ , the yield of tropane is doubled. T. M. L.

**Synthesis of Hygrie Acid.** By RICHARD WILLSTÄTTER (*Ber.*, 1900, 33, 1160—1166).—*Ethyl bromopropylmalonate*,



prepared by the action of trimethylene bromide on ethyl sodiomalonate, boils at  $158-160^{\circ}$  under 14 mm. pressure.

By the action of bromine, it is converted into *ethyl  $\alpha$ , $\delta$ -dibromopropylmalonate*,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CBr}(\text{CO}_2\text{Et})_2$ ; this boils at  $177^{\circ}$  under 11 mm. pressure, and, when treated with ammonia, gives an *amide*,

$\text{CH}_2\left\langle\begin{array}{c} \text{CH}_2\cdot\text{NH} \\ \text{CH}_2\cdot\text{C}(\text{CO}\cdot\text{NH}_2)_2 \end{array}\right\rangle$ , which crystallises in rhombic tablets, melts at  $163^{\circ}$ , and is hydrolysed by hydrochloric acid or baryta to 2-pyrrolidinecarboxylic acid which melts at  $198^{\circ}$ , gives an *ethyl ester* which boils at  $75-76^{\circ}$  under 11 mm. pressure, and closely resembles hygrie acid. The chief product of the action of methylamine is a *methylamide*,

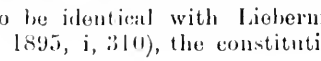
probably  $\text{CH}_2\left\langle\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{NMe}\cdot\text{CO} \end{array}\right\rangle\text{C}\left\langle\begin{array}{c} \text{CO}\cdot\text{NHMe} \\ \text{NHMe} \end{array}\right\rangle$ , which crystallises in monoclinic prisms, melts at  $124^{\circ}$ , and when hydrolysed with baryta loses only 1 mol. of methylamine, giving rise to a substance which is regarded as the lactam of  $\alpha$ , $\delta$ -dimethyldiaminovaleric acid, a methylaminomethyl-2-piperidone,  $\text{CH}_2\left\langle\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{NMe}\cdot\text{CO} \end{array}\right\rangle\text{CH}\cdot\text{NHMe}$ . The pyrrolidino compound is only produced in small quantities by the action of methylamine, but was isolated in the form of *ethyl 1-methylpyrrolidine-2:2-dicarboxylate*,

$\left\langle\begin{array}{c} \text{CH}_2\cdot\text{NMe} \\ \text{CH}_2\cdot\text{CH}_2 \end{array}\right\rangle\text{C}(\text{CO}_2\text{Et})_2$ , which boils at  $133-135^{\circ}$  under 16 mm. pressure; from the product of hydrolysis, there was also isolated 1-methylpyrrolidine-2-carboxylic acid,  $\left\langle\begin{array}{c} \text{CH}_2\cdot\text{NMe} \\ \text{CH}_2\cdot\text{CH}_2 \end{array}\right\rangle\text{CH}\cdot\text{CO}_2\text{H}$ ,

which was found to be identical with Liebermann and Cybulski's hygrie acid (*Abstr.*, 1895, i, 310), the constitution of which is thus finally established.

T. M. L.

**Action of Phenylcarbimide and Aniline on  $\gamma$ -Ketonic Acids.**—By TIMOTHÉE KLOBE (*Compt. rend.*, 1900, 130, 1254—1256. Compare *Abstr.*, 1899, i, 510).—When tolylbutanoic acid,



is heated at  $200^{\circ}$  with phenylcarbimide, the compound  $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_2$ , a

polymeride of the pyrrolone  $C_7H_{15}NO$ , is produced, together with a small amount of the *anilide* of the acid. The former substance crystallises in golden-yellow needles melting at  $204^\circ$ , and the latter in nacreous leaflets melting at  $147^\circ$ .

Triphenylbutenolide (triphenylcrotonolactone),  $CH \begin{smallmatrix} \text{CPh-O} \\ \text{CPh}_2 \cdot \text{CO} \end{smallmatrix}$ , obtained by heating triphenylbutanonoic acid,  $COPh \cdot CH_2 \cdot CPh_2 \cdot CO_2H$ , with the same reagent at  $100^\circ$ , is identical with the substance obtained by Japp and Klingemann (Trans., 1890, 57, 678).

Tetraphenylpyrrolone,  $CH \begin{smallmatrix} \text{CPh-NPh} \\ \text{CPh}_2 \cdot \text{CO} \end{smallmatrix}$ , prepared by heating triphenylbutanonoic acid with aniline in sealed tubes at  $180-200^\circ$ , crystallises from benzene in monoclinic prisms containing 1 mol. of the solvent, and melting at  $115^\circ$ . The compound is dimorphous, for it crystallises from alcohol both in hexagonal and monoclinic prisms, the former melting at  $123-124^\circ$ , the latter at  $133-134^\circ$  (compare Tutton, Trans., 1890, 57, 714).

The  $\gamma$ -lactone,  $COPh \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CO-O} \\ \text{CH} \cdot \text{CPh} \end{smallmatrix}$ , of diphenacylacetic acid,  $CH(CH_2 \cdot COPh)_2 \cdot CO_2H$ , produced from this substance with phenylcarbimide, melts at  $162^\circ$ ; when heated with carbanilide, it is decomposed without yielding either an anilide or a pyrrolone. The latter, 1:2-diphenyl-4-phenacylpyrrolone,  $COPh \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CO} \cdot \text{NPh} \\ \text{CH} \cdot \text{CPh} \end{smallmatrix}$ , is obtained by the direct action of aniline on the acid; it melts at  $140^\circ$ . A polymeride,  $C_{48}H_{38}O_4N_2$ , of this pyrrolone is sometimes obtained in this condensation; it is a well-defined, red substance, which, when crystallised from alcohol, undergoes a partial transformation into a colourless derivative melting at  $280^\circ$  and having an acid reaction.

G. T. M.

Addition of Formaldehyde to 2:4-Lutidine. Decomposition of 2:4-Lupetidine into its Optical Isomerides. By OTTO ENGELS (Ber., 1900, 33, 1087—1090).—When 2:4-lutidine is heated with 40 per cent. formaldehyde solution at  $135-140^\circ$ , 2:4-lutidylalkine [2-hydroxyethyl-4-methylpyridine],  $CH \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CH} = \text{N} \end{smallmatrix} \text{C} \cdot CH_2 \cdot CH_2 \cdot OH$ , is formed. This boils at  $130-132^\circ$  under 16 mm. pressure; its *platini-chloride* and *aurichloride* were analysed.

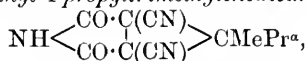
Inactive 2:4-lupetidine, obtained by reducing 2:4-lutidine with sodium and absolute alcohol, was mixed with the equivalent amount of *a*-tartaric acid in aqueous solution, and the solution concentrated; crystals melting at  $49-50^\circ$  separated, and from these the *d*-lupetidine was obtained, with a specific rotation  $[\alpha]_D + 23.17^\circ$ . By regenerating the base from the mother liquor and treating it with *l*-tartaric acid, a salt was obtained which melted at  $49-50^\circ$ ; from this, the *l*-lupetidine was isolated with a specific rotation  $[\alpha]_D - 21.0^\circ$ .

C. F. B.

Synthesis of Glutaric and Trimethylene Derivatives. By A. MINOZZI (Gazzetta, 1900, 30, i, 265—278. Compare Guareschi and Grande, this vol., i, 111; and Pasquali, Abstr., 1898, i, 272).—

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-propylpiperidine (aa-dicyano-ββ-methylpropylglutarimide),  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{CN}) \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} > \text{CMePr}^{\alpha}$ , obtained as its ammonium derivative by the action of methyl propyl ketone on ethyl cyanoacetate in presence of alcoholic ammonia, separates from acetic acid in fine, large, transparent laminae melting at 201—202°; it gives a yellow coloration with potassium nitrite and sulphuric acid, and is soluble in alcohol or ether, or in boiling water, to which it gives an acid reaction. Its ammonium salt,  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_4$ , is a white, crystalline compound soluble in water; it loses ammonia even at the ordinary temperature, and melts and decomposes at 192—193°; the aqueous solution loses hydrogen cyanide and propane slowly on standing, more quickly on heating, with the formation of the ammonium derivative of methylidicyanoglutarimide, crystallising in beautiful needles, which on heating lose ammonia, and do not melt at 310°. The silver salt,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_3\text{Ag}$ , is a white, flocculent precipitate. The dibromo-derivative,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3\text{Br}_2$ , is a white compound soluble in boiling water, alcohol, or 50 per cent. acetic acid; on heating, it loses bromine and melts and decomposes at 170—173°.

3 : 5-Dicyano-4-methyl-4-propyltrimethylenedicarbonimide,



obtained on heating the dibromo-derivative with 50 per cent. acetic acid, crystallises from acetic acid in thin, white plates, or from water in hard, colourless needles, begins to decompose at 175°, melts at 183°, gives an acid aqueous solution, yields no coloration with potassium nitrite and sulphuric acid, but forms soluble salts with the alkali and alkaline earth metals, and with mercuric chloride and lead acetate gives white, flocculent precipitates insoluble in boiling water. Its silver salt,  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_3\text{Ag}$ , is a white, flocculent precipitate which is turned brown by light, and decomposes in boiling water. On hydrolysing the imide with aqueous sodium hydroxide, ammonia is evolved, and the sodium salt of 1-methyl-1-propyltrimethylene-2 : 3-dicyanodicarboxylic acid,  $\text{CMePr}^{\alpha} \begin{smallmatrix} \text{C}(\text{CN}) \cdot \text{CO}_2\text{H} \\ \text{C}(\text{CN}) \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , formed; the acid separates from alcohol in a crystalline mass melting at 116—119°; its silver salt,  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2\text{Ag}_2$ , forms a white, gelatinous mass readily decomposable by the action of light or heat.

The action in the cold of methyl isopropyl ketone (1 mol.) on ethyl cyanoacetate (2 mols.) in presence of alcoholic ammonia (3 mols.) gives rise to cyanoacetamide, but if aqueous ammonia is employed, or if the above mixture is heated at 85—90° in a reflux apparatus, 3 : 5-dicyano-2 : 6-dioxy-4-methyl-4-isopropylpiperidine (aa-dicyano-ββ-methylisopropylglutarimide),  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{CN}) \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} > \text{CMePr}^{\beta}$ , is obtained; it separates from dilute hydrochloric acid in flocculent aggregates of minute, white needles, or from alcohol in large, colourless, transparent plates melting at 232—234°, and is soluble in glacial acetic acid, and to a slight extent in water, forming an acid solution. Its ammonium salt is unstable, the aqueous solution decomposing with the formation of

the ammonium salt of methyldicyanoglutarimide and evolution of propane. The *silver* salt,  $C_{11}H_{12}O_2N_3Ag$ , forms a white, flocculent precipitate. The *dibromo*-derivative,  $C_{11}H_{11}O_2N_3Br_2$ , separates from water in flocculent masses of small, white needles melting and decomposing at  $163-165^\circ$ ; it dissolves in alcohol, ether, or acetic acid. 3:5-Dicyano-4-methyl 4-isopropyltrimethylenedicarbonimide,  $C_{11}H_{11}O_2N_3$ , which is obtained on heating the bromo-derivative with dilute acetic acid, separates in brilliant, colourless prisms melting and decomposing at about  $240^\circ$ ; it dissolves slightly in water, giving an acid solution which gives no coloration with potassium nitrite and sulphuric acid, and does not yield any gas when neutralised with ammonia. Its *silver* salt,  $C_{11}H_{10}O_2N_3Ag$ , is a white, flocculent precipitate which is moderately soluble in water and is decomposed by the action of light or heat.

T. H. P.

**2-Methylketole.** By R. VON WALTHER and J. CLEMEN (*J. pr. Chem.*, 1900, [ii], 61, 249-289).—2-Methylketole condenses with aldehydes to

form well-characterised compounds of the type  $CHR\left(C\begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > NH\right)_2$ .

*Methylene-bis-2-methylketole* is a white, microcrystalline powder which melts at  $230-231^\circ$ ; *p-methoxybenzylidene-bis-2-methylketole* is a faint reddish, microcrystalline powder which melts at  $206^\circ$ ; *o-hydroxybenzylidene-bis-2-methylketole* is a white, crystalline powder which melts at  $224^\circ$ ; *isopropylbenzylidene-bis-2-methylketole* is a white, microcrystalline powder which melts at  $220^\circ$  and turns red on exposure to light; *p-nitrobenzylidene-bis-2-methylketole* is a yellowish-red, microcrystalline powder which melts at  $236^\circ$ ; and *o-nitrobenzylidene-bis-2-methylketole* is a yellowish, microcrystalline powder which melts at  $229^\circ$ .

Ethyl acetoacetate condenses with 2-methylketole to form the *compound*,  $CO_2Et \cdot CH_2 \cdot CMe\left(C\begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > NH\right)_2$ , which is a pale yellow, amorphous powder melting at  $158^\circ$ . Phenylcarbimide and 2-methylketole condense to form the *compound*,  $CH\begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > N \cdot CO \cdot NHPh$ , which forms silvery leaflets melting at  $170^\circ$ . *Mononitro-2-methylketole*, best prepared by the action of a mixture of 100 per cent. nitric acid and concentrated sulphuric acid on 2-methylketole, forms compact, yellow prisms which melt at  $170^\circ$ ; it condenses with formaldehyde to *methylene-bis-nitro-2-methylketole*, which is a yellow, microcrystalline powder melting at  $131^\circ$ , and with benzaldehyde to *benzylidene-bis-nitro-2-methylketole*, which is a yellow, microcrystalline powder melting at  $291^\circ$ .

When heated with nitric acid of sp. gr. 1.38, 2-methylketole yields *dinitro-2-methylketole*, which forms brownish-yellow, lustrous, microcrystalline powder melting at  $268^\circ$ , and a brown, amorphous *substance* melting at  $277-278^\circ$ . Nitro-2-methylketole is only attacked with great difficulty by reducing agents; treatment with tin and hydrochloric acid for 3 hours gives a small yield of *amino-2-methylketole*; this is precipitated from benzene by light petroleum in the form of a colourless, light, voluminous substance, which melts at  $137^\circ$  and yields an amorphous *acetyl* derivative melting at  $188^\circ$ . 2-Methylketolephenylcarbamide and

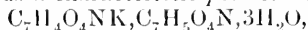
2-methylketolephenylthiocarbamide are white, amorphous powders which melt respectively at  $194^{\circ}$  and  $162^{\circ}$ . R. H. P.

**2-Methylpyridine-6-carboxylic Acid.** By ALBERT LADENBURG and K. SCHOLTZE (*Ber.*, 1900, 33, 1081).—2-Methylpyridine-6-carboxylic acid,  $C_7H_7O_2N$ , is prepared by oxidising 2:6-lutidine with three times its weight of potassium permanganate in 3 per cent. solution at  $50-60^{\circ}$ , and is isolated by means of its copper salt. It crystallises in colourless, lustrous needles, and is readily soluble even in cold water. The air-dried substance contains  $1H_2O$  and melts at  $95^{\circ}$ . The copper salt,  $(C_7H_6NO_2)_2Cu, H_2O$ , forms bright blue, well-formed crystals, is sparingly soluble in hot water, and decomposes at  $252-253^{\circ}$ .

A. L.

**Pyridinecarboxylic Acids.** By ADOLF PINNER (*Ber.*, 1900, 33, 1225—1230).—The author has examined fractions of pyridine bases of different boiling points obtained from coal tar, by oxidising them with aqueous potassium permanganate and separating the mixed carboxylic acids by means of their copper salts, according to Weidel's method. The fraction boiling at  $128-134^{\circ}$  consists almost entirely of  $\alpha$ -picoline, and can be used as a source of  $\alpha$ -picolinic acid; that boiling at  $137-142^{\circ}$  contains only a small quantity of  $\alpha$ -picoline, with larger, almost equal, quantities of  $\beta$ - and  $\gamma$  picoline, along with much 2:6-dimethylpyridine; this fraction can be used as a source of nicotinic and isonicotinic acids.

The hitherto undescribed 2-methylpyridine-6-carboxylic acid, obtained in the oxidation of the fraction boiling at  $135-142^{\circ}$ , is characterised by its great solubility in water and alcohol, and can be purified by crystallisation from benzene (see following abstract). Pyridine-2:6-dicarboxylic acid yields a characteristic potassium salt,



which forms beautiful, long, slender needles.

The esters of pyridinecarboxylic acids combine readily with ethyl acetate in presence of sodium ethoxide to form crystalline sodium derivatives of the type  $C_5NH_4 \cdot C(ONa) \cdot CH \cdot CO_2Et$ ; ethyl  $\alpha$ - and  $\beta$ -pyridoylacetates, obtained from the corresponding sodium derivatives, are oils which decompose on distillation under reduced pressure; ethyl  $\gamma$ -pyridoylacetate, on the other hand, is a solid which can readily be purified. These compounds will be dealt with in a subsequent communication.

W. A. D.

**2-Methylpyridine-6-carboxylic Acid.** By ADOLF PINNER and J. LEWIN (*Ber.*, 1900, 33, 1230—1231).—This acid (preceding abstract) forms long, white, lustrous needles, and melts at  $81-85^{\circ}$ ; the hydrochloride forms leaflets melting at  $138^{\circ}$ , and the acid sulphate,  $C_7H_7O_2N, H_2SO_4$ , highly lustrous, hexagonal prisms, sparingly soluble in cold alcohol. The barium salt forms shining leaflets; the copper salt, with  $2H_2O$ , forms beautiful, bluish green, pointed prisms, whilst with  $1H_2O$  it crystallises in blue plates. The acid on oxidation yields pyridine-2:6-dicarboxylic acid.

W. A. D.

**Conversion of Diethyl Lutidinedicarboxylate into Diaminolutidine.** By ERNST MOHR (*Ber.*, 1900, 33, 1111—1120).—The

*dihydrazide*,  $C_5NHMe_2(CO \cdot NH \cdot NH_2)_2$ , obtained by warming ethyl lutidinedicarboxylate [ $Me_2 : (CO_2Et)_2 = 2 : 6 : 3 : 5$ ] (Knoevenagel and Klages, *Annalen*, 1894, 281, 94) with hydrazine hydrate, crystallises from alcohol in thin, colourless prisms, and melts with slight decomposition at  $228^\circ$ ; from water, needles with  $1H_2O$  are obtained; the *hydrochloride*,  $C_9H_{13}O_2N_5 \cdot 3HCl \cdot H_2O$ , melts and decomposes at  $251^\circ$ . The  $\beta$ -*propylidene* (acetone) derivative,  $C_5NHMe_2(CO \cdot NH \cdot N : CMe_2)_2$ , is a white powder which melts and decomposes at  $298^\circ$ ; the analogous *dibenzylidene* derivative,  $C_{23}H_{21}O_2N_5$ , crystallises from glacial acetic acid, and does not melt at  $300^\circ$ . *Lutidinedicarboxylodiazoinide*,  $C_5NHMe_2 \left( CO \cdot N < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} \right)$ , obtained by the action of nitrous acid at  $0^\circ$

on the foregoing hydrazide, is a white powder which explodes at  $79-80^\circ$ , and, when heated with absolute alcohol, yields \**diurethyl-lutidine*,  $C_5NHMe_2(NH \cdot CO_2Et)_2$ ; this forms stout, transparent prisms, melts at  $157^\circ$ , and on being heated with hydrochloric acid for 5 hours at  $100-120^\circ$ , yields *diaminolutidine dihydrochloride*,  $C_5NHMe_2(NH_2)_2 \cdot 2HCl \cdot H_2O$  [ $Me_2 : (NH_2)_2 = 2 : 6 : 3 : 5$ ]. This, salt when heated at  $110^\circ$ , gives rise to the *hydrochloride*,  $C_7H_{11}N_3 \cdot HCl$ , which darkens at  $265^\circ$ , and melts and decomposes at  $275-280^\circ$ ; on crystallising the dihydrochloride from boiling water, long, slender, felted needles of the *salt*,  $C_7H_{11}N_3 \cdot HCl \cdot H_2O$ , are obtained, which blacken at  $280^\circ$  and melt and decompose at  $290^\circ$ . The *base*,  $C_5NHMe_2(NH_2)_2$ , crystallises from benzene in feebly yellow prisms, and melts at  $169-170^\circ$ .

W. A. D.

**Solubilities of Osazones.** By CARL NEUBERG (*Zeit. Physiol. Chem.*, 1900, 29, 274-280).—It is a well-known fact that it is impossible to isolate from diabetic urine an amount of phenyl-glucosazone corresponding with the amount of sugar determined by polarimetric or titrimetric methods. The author concludes that this is due to the fact that the osazones are more soluble in liquids rich in nitrogen compounds than they are in water. This has been proved in the case of the amount of osazone from dextrose and from lævulose. According to Maquenne (*Abstr.*, 1891, 1142), in one hour at  $100^\circ$  under fixed conditions 1 gram of dextrose yields 0.32, and the same amount of lævulose 0.72, gram of osazone; the author finds that, when the same conditions are employed, with the exception that urine is used instead of water for washing, 1 gram of dextrose yields 0.186 gram of osazone and 1 gram of lævulose 0.432 gram of osazone.

Further experiments have shown that ammonia, amines, ammonium compounds, and most nitrogen derivatives increase the solubility of osazones in water or in alcohol.

In the estimation of sugars in urine, etc., it is therefore advisable to remove as far as possible the nitrogen compounds before precipitating with phenylhydrazine. Amino-acids, &c., can usually be removed in the form of silver, lead, or copper salts, and carbamide by the careful addition of alkali nitrate and acetic acid.

J. J. S.

\* The author suggests the name *urethyl* for the radicle  $\cdot NH \cdot CO_2Et$ .



**Hydrazones of Dithiocarbonates.** By MAX BUSCH and EDMUND LINGENBRINK [and in part H. HOLZMANN] (*J. pr. Chem.*, 1900, [ii], 61, 336—344. Compare this vol., i, 66). The *phenylhydrazone* of *methyl o-nitrobenzyl dithiocarbonate* forms large, lustrous, orange-coloured needles, which melt at 60—61°. The *diphenylhydrazone* of *dimethyl methylene dithiodicarbonate*, obtained by the action of ethylene dibromide on methyl phenyldithiocarbazine, forms lustrous, brittle needles which melt at 113—114°. The corresponding *p*-tolyl-hydrazones are oils.

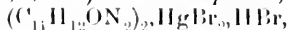
Potassium *p*-bromophenyldithiocarbazine reacts with methyl iodide, forming *methyl p-bromophenyldithiocarbazine*, which crystallises in small needles melting at 158—159°, and on treatment with methyl iodide yields the *p-bromophenylhydrazone* of *dimethyl dithiocarbonate*, which forms compact, brownish crystals melting at 48—49°. The *p-bromophenylhydrazone* of *ethylene dithiocarbonate* forms small, colourless needles melting at 141°. *Methyl hydrogen benzoylphenyldithiocarbazine* forms lustrous, small needles, which turn brown at 200°, melt and froth at 202°; on treatment with methyl iodide, it yields the *benzoylphenylhydrazone* of *dimethyl dithiocarbonate*, which crystallises in four-sided columns melting at 110—111°. *Benzyl acetylphenyldithiocarbazine* crystallises in small, yellow needles melting at 154°, and yields an oil on treatment with methyl iodide.

The phenylhydrazone of ethylene dithiocarbonate, on hydrolysis with dilute sulphuric acid, yields ketomethylene ethylene disulphide (Husemann, *Annalen*, 1863, 126, 269), which softens at 35° and melts at 39° (not 31°).  
R. H. P.

**Action of  $\alpha$ -Acylated Phenylhydrazines on the Chlorine Derivatives of Quinones.** By WILLIAM MCPHERSON and ROBERT FISCHER (*J. Amer. Chem. Soc.*, 1900, 22, 141—144).— *$\alpha$ -Benzoylphenylhydrazinotrichloroquinone*,  $C_6Cl_3O_2 \cdot NH \cdot NBzPh$ , obtained by the action of  $\alpha$ -benzoylphenylhydrazine on trichloroquinone, crystallises in bright red, rectangular prisms, is readily soluble in hot benzene or alcohol, sparingly so in light petroleum, and melts at 158.5°. It reacts with phenylhydrazine, but decomposition occurs with evolution of gas. By the action of concentrated sulphuric acid or alcoholic potassium hydroxide, the benzoyl group is eliminated, and a crystalline product obtained which is soluble in sodium hydroxide and melts and decomposes at 198°.

$\alpha$ -Benzoylphenylhydrazinotrichloroquinone is also produced when  $\alpha$ -benzoylphenylhydrazine is heated with tetrachloroquinone, hydrogen chloride being evolved.  
E. G.

**New Mercuric Haloid Derivatives of Antipyrine.** By JULES VILLE and CHARLES ASTRE (*Compt. rend.*, 1900, 130, 1256—1258. Compare Abstr., 1898, i, 482).—The compound,



produced by adding dilute acetic acid to an aqueous solution of mercuric and potassium bromides and antipyrine, crystallises in lamelle and rhombohedral plates, melts at 115—116°, and is slightly soluble in water, alcohol, or chloroform. Concentrated sulphuric

acid, alone or mixed with manganese dioxide, causes an evolution of hydrogen bromide, but bromine is not liberated. The compound ( $C_{11}H_{12}ON_2$ )<sub>2</sub>.HgI<sub>2</sub>.HI, obtained in a precisely similar manner, melts at 119—120°, and is very slightly soluble in water, dissolving somewhat more readily in alcohol and chloroform. When treated with excess of water, it is partly decomposed with the precipitation of red mercuric iodide. Concentrated sulphuric acid causes the liberation of iodine.

G. T. M.

**New Synthesis in the Quinazoline Group.** By MARSTON T. BOGERT and AUGUST H. GOTTHELF (*J. Amer. Chem. Soc.*, 1900, 22, 129—132).—By the action of acetonitrile on anthranilic acid, Mathews (Abstr., 1899, i, 57) obtained a crystalline product melting at 232°. The authors have identified this substance as the 2-methyl-4-keto-dihydroquinazoline first described by Weddige (Abstr., 1885, 661, and 1887, 1044), and have extended the reaction to the preparation of the corresponding 2-ethyl-, 2-phenyl-, 2-benzyl-, and 2-*p*-tolyl-derivatives. The three last will be described later.

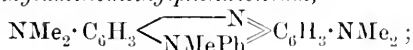
E. G.

**Reactions in which Saffranines are formed.** By D. HARDIN (*Ber.*, 1900, 33, 1212—1218).—A dilute neutral aqueous solution of *p*-diaminodiphenylamine sulphate (1 mol.) and the hydrochloride of a monamine (1 mol.) was heated with a little oxalic acid and oxidised with manganese dioxide. Under these circumstances the following amines yielded saffranines: Aniline, *o*-, *m*-, and *p*-toluidines, 1:2:4- and 1:3:4-xylydines, 2:4:5-trimethylaniline, 2:3:4:5- and 2:3:4:6-tetramethylanilines, and pentamethylaniline. 1:2:3-, 1:4:3-, 1:3:2-, and 1:3:5-Xylydines, 2:4:6-, 3:4:5-, 2:3:4- (?) and 2:3:5-trimethylanilines, and 2:3:5:6-tetramethylaniline do not form saffranines under the same conditions. From this it appears that a saffranine is formed when one methyl group is attached to the benzene nucleus of the amine, whatever the position of the group relatively to the amino-group; that when two or more methyl groups are present one must be in the para-position if a saffranine is to be formed, and that the rest must be in pairs occupying para-positions relatively to each other, the position of an odd one left over being indifferent.

In some cases, a saffranine is formed when *p*-phenylenediamine (1 mol.) and a monamine (2 mols.) are oxidised together. If an indamine is formed as a first stage in the production of the saffranine, it might be expected that the para-position in the amine ought not to be occupied, as in the opposite case the formation of an indamine is impossible. As a matter of fact, it was found that *m*-toluidine does form a saffranine with *p*-phenylenediamine and 1:2:4-xylydine does not. 1:3:2- and 1:4:3-Xylydines, however, yield an indamine, but no saffranine.

Nitrosodimethylaniline hydrochloride forms a saffranine when it is heated with a monamine (1 mol. of each) in alcoholic solution; and it might be thought that those amines which do not form a saffranine with *p*-phenylenediamine would form none with nitrosodimethylaniline. Although, however, *p*-toluidine does not form a saffranine, it is found that 1:3:2-, 1:4:3-, and 1:2:3-xylydines do so. Consequently the saffra-

nines are formed in this case without the intermediate formation of an indamine, and it is necessary for their formation that the para-position should not be occupied. From nitrosodimethylaniline and dimethylaniline a monacid base was obtained which is probably *B<sub>1</sub>-4-dimethyl-amino-B<sub>2</sub>-4-dimethylaminomethylphenazonium*,



its *mercurichloride* was analysed.

Suggestions are made as to the course of the reaction in which a safranine is formed; for these, the original must be consulted.

C. F. B.

**Action of Thiocynoacetic Acid on Phenylhydrazine.** By CARL D. HARRIES and ERNST KLAMT (*Ber.*, 1900, **33**, 1152—1160).—*Aniliminocarbaminothioglycollic acid*,  $\text{NHPh} \cdot \text{N} : \text{C}(\text{NH}_2) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared by the action of phenylhydrazine on thiocynoacetic acid (Claesson, *Abstr.*, 1878, 37), crystallises from boiling alcohol and melts at  $149^\circ$ ; the substance has no marked basic properties and a nitroso-derivative could not be prepared. *Methylaniliminocarbaminothioglycollic acid*,  $\text{NMePh} \cdot \text{N} : \text{C}(\text{NH}_2) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared by the action of *as*-phenylmethylhydrazine on thiocynoacetic acid, melts at  $146^\circ$  and resembles the preceding acid.

*Phenylaminopyridothiazinone*,  $\text{CO} \begin{array}{c} \text{NPh} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{S} \end{array} \text{C} \cdot \text{NH}_2$ , prepared by heating aniliminocarbaminothioglycollic acid above its melting point, or by heating ethyl thiocynoacetate (Heintz, *Annalen*, 1865, **136**, 223) with phenylhydrazine, crystallises from alcohol in colourless prisms and melts at  $176^\circ$ ; the *hydrochloride* crystallises in needles and melts at  $190^\circ$ ; the violet *potassium* salt crystallises in pearly prisms, and is regarded as derived from a hydroxylic modification of the base.

*Phenyldiazopyridothiazinone*,  $\text{CO} \begin{array}{c} \text{NPh} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{S} \end{array} \text{C} \cdot \text{N} : \text{N} \cdot \text{OH}$ , prepared by the action of nitrous acid on the preceding compound, is a white, crystalline substance which blackens at  $75^\circ$  and melts with decomposition at  $130^\circ$ ; it does not give Liebermann's reaction, and could not be converted into the thiazole by boiling with alcohol.

*Diaminocarbiminothioglycollic acid*,  $\text{NH}_2 \cdot \text{N} : \text{C}(\text{NH}_2) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises in white needles and melts at  $92^\circ$ . By boiling with water, it is converted into an *anhydride*, probably  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{S} \end{array} \text{C} \cdot \text{NH}_2$ , which separates in white prisms and melts at  $277^\circ$ . T. M. L.

**Action of Methyl Iodide on Dithiodiazolone Disulphides; Decomposition of Thiodiazolones.** By MAX BUSCH and EDMUND LINGENBRINK (*J. pr. Chem.*, 1900, [ii], **61**, 330—335).—Phenyldithiodiazolone disulphide (*Abstr.*, 1894, i, 625), on treatment with methyl iodide in alcoholic solution, yields phenylthiodiazolone methosulphide (E. Wolpert, *Inaug. Diss. Erlangen*, 1899, 35), which, when warmed with ethyl alcoholic potash, gives *methyl ethyl phenyldithiocarbazinic a-carboxylate*,  $\text{SH} \cdot \text{C}(\text{SMe}) : \text{N} \cdot \text{NPh} \cdot \text{CO}_2\text{Et}$ , which crystallises in prisms

melting at  $101^{\circ}$ , and can also be prepared by the action of ethyl chlorocarbonate on methyl phenyldithiocarbazinate. The corresponding *methyl* compound, obtained when the methosulphide is decomposed by methyl alcoholic potash, crystallises in six-sided prisms melting at  $114^{\circ}$ . *p*-Tolythiodiazolone methosulphide (Wolpert, *loc. cit.*) is obtained in a similar manner from *p*-tolyldithiodiazolone disulphide, and on treatment with ethyl alcoholic potash yields *methyl ethyl p-tolyl-carbazinic- $\alpha$ -carboxylate*, which crystallises in silvery needles or prisms melting at  $111^{\circ}$ .  
R. H. P.

**Products of the Action of Hydrazine on Thiocarbamides.** By MAX BUSCH and PAUL BAUER (*Ber.*, 1900, 33, 1058—1073).—Thiocarbanilide reacts with hydrazine hydrate in alcoholic solution, yielding 4-phenylsemicarbazide and aniline; in presence of alcoholic potash, however, potassium hydrosulphide and a substituted aminoguanidine are produced.

*Aminodiphenylguanidine*,  $\text{NPh}\cdot\text{C}(\text{NHPh})\cdot\text{NH}\cdot\text{NH}_2$ , is obtained by heating thiocarbanilide with a large excess of hydrazine hydrate and alcoholic potash in closed tubes at  $110$ — $115^{\circ}$ , but is accompanied by large quantities of its aniline-additive product, diphenylcarbamide, and a basic substance melting at  $232^{\circ}$ . It separates from a mixture of ether and light petroleum in crusts of compact crystals, sinters at  $96^{\circ}$ , melts at  $98$ — $99^{\circ}$ , decomposes at  $180^{\circ}$ , and is somewhat readily soluble in the common media with the exception of light petroleum and water. From benzene, crystals having the composition  $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{C}_6\text{H}_6$  are obtained. It combines with aniline to form a substance,  $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{C}_6\text{H}_7\text{N}$ , whose properties have already been described (this vol., i, 27); the corresponding *compound*, with *p*-toluidine,  $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{C}_7\text{H}_9\text{N}$ , crystallises in white needles and melts at  $108^{\circ}$ . It does not combine with  $\alpha$ - or  $\beta$ -naphthylamine. *Aminodiphenylguanidine nitrate*,  $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{HNO}_3$ , forms quadratic tables, and melts at  $184$ — $186^{\circ}$ . The *sulphate* melts indefinitely at  $95^{\circ}$ . The *hydrochloride* forms slender, white needles. The *picrate* is deposited from ether in yellow leaflets containing  $\frac{1}{2}$  mol. of the solvent and melting at  $135^{\circ}$ . The *oxalate* forms leaflets and melts and decomposes at  $209$ — $210^{\circ}$ .

*Benzylidenaminodiphenylguanidine*,  $\text{NPh}\cdot\text{C}(\text{NHPh})\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$ , dissolves readily in the usual media, crystallises from dilute alcohol in yellowish needles, and melts at  $121$ — $122^{\circ}$ . The *nitrate* forms lustrous, transparent, compact needles, and melts at  $157^{\circ}$ . The *m-nitro*-derivative forms intensely yellow, lustrous needles, melts at about  $130^{\circ}$ , and is readily soluble in ether or benzene.

*Thiocarbanilinoaminodiphenylguanidine*,  
 $\text{NPh}\cdot\text{C}(\text{NHPh})\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ ,  
forms silky needles melting at  $137^{\circ}$ , and separates from benzene in snow-white needles which contain the solvent and melt at about  $90^{\circ}$ .

*5-Anilino-4-phenyltriazole*,  $\text{N} \begin{smallmatrix} \text{N}=\text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{NHPh}) \end{smallmatrix} \text{NPh}$ , prepared by heating aminodiphenylguanidine with formic acid, separates from alcohol in long, slender, silky needles, melts at  $213^{\circ}$ , has markedly basic properties, and dissolves readily in boiling alcohol, chloroform,

or dilute mineral acids, but does not form a stable acetate. It is not affected by nitrous acid or by concentrated hydrochloric acid at  $220^{\circ}$ , but is suddenly decomposed at higher temperatures. The *acetyl* derivative,  $C_{14}H_{11}N_4Ac$ , melts at  $170-171^{\circ}$ .

5-Anilino-4-phenyl-3-methyltriazole,  $N \begin{smallmatrix} \diagup N=CMe \\ \diagdown C(NHPh) \end{smallmatrix} > NPh$ , from aminodiphenylguanidine and acetic anhydride, is readily soluble in alcohol; it separates from benzene in lustrous, flat needles or leaflets melting at  $227-228^{\circ}$ . The *hydrochloride*,  $C_{15}H_{14}N_4 \cdot HCl$ , forms white needles.

*Benzoylamino*diphenylguanidine,  $NPh : C(NHPh) \cdot NH \cdot NHBz$ , separates from alcohol in beautiful transparent needles which melt with effervescence at  $173^{\circ}$ ; it dissolves in mineral acids and forms a sparingly soluble *sulphate*, which forms needles melting at  $221-222^{\circ}$ .

5-Anilino-3:4-diphenyltriazole,  $N \begin{smallmatrix} \diagup N=CPh \\ \diagdown C(NHPh) \end{smallmatrix} > NPh$ , formed when the foregoing substance is heated above its melting point, separates from alcohol in large, transparent prisms, dissolves readily in acetic acid and chloroform, and melts at  $210-211^{\circ}$ ; the *hydrochloride*,  $C_{20}H_{16}N_4 \cdot HCl$ , forms white needles melting at  $220-223^{\circ}$ , and is dissociated in water.

*Phenylimino*phenyltetrazolone,  $\begin{smallmatrix} N \cdot NPh \\ | \\ N-NH \end{smallmatrix} > C : NPh$ , prepared from aminodiphenylguanidine by the action of nitrous acid, separates from alcohol in shining, slender needles, melts at  $162-163^{\circ}$  and decomposes at  $220^{\circ}$ , is readily soluble in warm alcohol, benzene, or chloroform, and has feebly acid properties, forming salts with alkalis which are decomposed by water. The *acetyl* derivative,  $C_{15}H_{13}ON_5$ , separates from dilute alcohol in transparent, compact crystals and melts at  $85-89^{\circ}$ .

*Aminodi-o-tolylguanidine*,  $C_7H_7N : C(NH \cdot C_7H_7) \cdot NH \cdot NH_2$ , prepared from di-*o*-tolylthiocarbamide and hydrazine, separates from alcohol in shining needles melting at  $120^{\circ}$ , and dissolves readily in the ordinary media, with the exception of petroleum. The *nitrate*, melting at  $118-119^{\circ}$ , and the *sulphate* are described.

*Benzyliden*aminodi-*o*-tolylguanidine,  
 $C_7H_7 \cdot N : C(NH \cdot C_7H_7) \cdot NH \cdot N : CHPh$ ,  
 crystallises from alcohol in aggregates of yellowish needles melting at  $125-126^{\circ}$ .

5-*Toluidino*-4-*o*-tolyl-3-methyltriazole,  $\begin{smallmatrix} C_7H_7 \cdot N \cdot CMe \\ | \\ C_7H_7 \cdot NH \cdot C=N \end{smallmatrix} > N$ , prepared from aminoditolylguanidine and acetic anhydride, crystallises from benzene in small, lustrous prisms and melts indefinitely at  $172-175^{\circ}$ .

*o*-Tolylimino-*o*-tolyltetrazolone,  $N \begin{smallmatrix} \diagup N(C_7H_7) \\ \diagdown N-NH \end{smallmatrix} > C : N \cdot C_7H_7$ , forms white, shining needles and melts at  $152^{\circ}$ .

*Aminodi-p-tolylguanidine* crystallises from alcohol in beautiful, transparent prisms melting at  $152^{\circ}$ . The *benzylidene* derivative forms needles melting at  $123-124^{\circ}$  and is readily hydrolysed by acids. The *o*-hydroxybenzylidene compound,  $C_{15}H_{16}N_4 \cdot CH \cdot C_6H_4 \cdot OH$ , forms

yellowish needles and dissolves in alcoholic soda, forming an intensely yellow solution which, in presence of excess of alkali, deposits the *sodium* derivative in yellow leaflets.

*Thiocarbanilinoaminoditolylguanidine*,  
 $C_7H_7 \cdot N : C(NH \cdot C_7H_7) \cdot NH \cdot NH \cdot CS \cdot NHPh$ ,  
 forms white, silky leaflets melting at  $148^\circ$ .

*5-p-Toluidino-4-p-tolyltriazole*,  $C_7H_7 - N \cdot CH \begin{matrix} \searrow \\ \nearrow \end{matrix} N$ , prepared from aminoditolylguanidine and formic acid, crystallises in colourless leaflets melting at  $224$ .

*p-Tolylimino-p-tolyltetrazolone* crystallises in silky, slender, felted needles and melts at  $207^\circ$ .  
 A. L.

**A New Synthesis of Guanine and of Xanthine.** By WILHELM TRAUBE (*Ber.*, 1900, 33, 1371—1383. Compare E. Fischer, *Abstr.*, 1898, i, 48).—A mixture of *cyanoacetylguanidine*,  $NH : C(NH_2) \cdot NH \cdot CO \cdot CH_2 \cdot CN$ , and of *2:4-diamino-6-hydroxypyrimidine*,  $NH_2 \cdot C \begin{matrix} \searrow CH \cdot C(OH) \\ \nearrow N : C(NH_2) \end{matrix} N$ , is obtained by the action of sodium ethoxide and ethyl cyanoacetate on guanidine hydrochloride; the former crystallises out as the solution cools, and the pyrimidine derivative may be obtained on evaporating the mother liquor; neither compound has a definite melting point. The guanidine compound is readily converted into the isomeric diaminohydroxypyrimidine when warmed with hot dilute sodium hydroxide, and on the addition of dilute sulphuric acid the pyrimidine *sulphate*,  $(C_4H_6ON_4)_2 \cdot H_2SO_4 \cdot H_2O$ , crystallises out; the corresponding nitrate and hydrochloride are readily soluble. Sodium nitrite reacts with an aqueous solution of the sulphate, yielding a *nitroso*-derivative,  $C_4H_5O_2N_5$ ; this crystallises in small, rose-coloured needles, is sparingly soluble in the usual solvents, and possesses neither basic nor acidic properties. When reduced with ammonium sulphide, it yields *2:4:5-triamino-6-hydroxypyrimidine*, a diacid base which separates from water in practically colourless crystals; the *sulphate*,  $C_4H_7ON_5 \cdot H_2SO_4 \cdot H_2O$ , crystallises in small, colourless needles, and when heated with the equivalent amount of sodium formate, and 8—10 times its weight of anhydrous formic acid yields guanine, which, in its turn, can be converted into xanthine by Fischer's method.

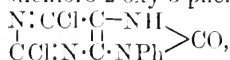
Cyanoacetylcarbamide (compare Mulder, *Abstr.*, 1879, 619) is best obtained by the action of carbamide on a mixture of cyanoacetic acid and phosphorus oxychloride; it crystallises from water in colourless crystals, and melts at  $209^\circ$ , and when treated with sodium hydroxide, and then with acetic acid, yields *4-amino-2:6-dihydroxypyrimidine*; this crystallises from water, has no definite melting point, and possesses both basic and acidic properties; when treated with nitrous acid, it yields an isonitroso-compound which, on reduction, gives *4:5-diamino-2:6-dihydroxypyrimidine*, the *sulphate* of which,  $(C_4H_6O_2N_4)_2 \cdot H_2SO_4 \cdot 1.5H_2O$ , is sparingly soluble in water. When boiled with formic acid (90 per cent.), it is converted into the *formyl* derivative,  $C_6H_6O_3N_4 \cdot \frac{1}{2}H_2O$ , which becomes anhydrous at  $150^\circ$ .

J. J. S.

**Aromatic Derivatives of Uric Acid.** By EMIL FISCHER (*Chem. Centr.*, 1900, i, 806—807; from *Sitzungsber. Akad. Wiss. Berlin*, 1900, 122—130).—By the action of phenyl cyanate in alkaline solution on uramil under conditions similar to those described by Paal (*Ber.*, 27, 974),  $\gamma$ -phenyl $\psi$ -uric acid,  $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}^{\text{H}}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh} \\ \text{CO}\cdot\text{NH}\cdot\text{CO} \end{array}$ , is formed.

This acid crystallises from 350 parts of water in aggregates of small needles; at 120°, it still retains  $\frac{1}{2}\text{H}_2\text{O}$ ; it chars at a higher temperature. It is almost insoluble in alcohol or ether, reduces ammoniacal silver solutions, and gives the murexide reaction. Carbon dioxide precipitates acid salts from alkaline solutions of the acid. The potassium, sodium, and ammonium salts are only slightly soluble in water, the potassium being less soluble than the sodium salt.

3-Phenyluric acid,  $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}^{\text{H}}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\cdot\text{C}^{\text{H}}\cdot\text{NPh} \end{array} > \text{CO}$ , prepared by boiling the pseudo-acid with dilute hydrochloric acid, crystallises from water with  $2\text{H}_2\text{O}$ , forming lustrous, silvery leaflets, or very small, thin, rectangular plates. At 320°, the acid becomes brown and chars at a higher temperature; it is more soluble in water than the corresponding methyluric acid, dissolving in about 120 parts of boiling water, and is very slightly soluble in alcohol. The potassium salt forms small prisms or plates, and the acid salt,  $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_4\text{K}$ , spherical aggregates of needles. The ammonium salt also crystallises in aggregates of small needles. 3-Phenyluric acid reduces ammoniacal silver solutions, is easily attacked by potassium permanganate or nitric acid, and by the action of chlorine forms alloxan and a crystalline compound which is probably a chloro-derivative of phenylcarbamide. By heating the acid with fuming hydrochloric acid at 170°, glycocine, ammonium chloride, and aniline are formed, and by the action of phosphorus oxychloride at 170°, 5 : 7-dichloro-2-oxy-3-phenylpurine,



is obtained, together with a compound which is insoluble in alkalis, and is probably phenyltrichloropurine. Phenylxydichloropurine crystallises from glacial acetic acid in small, flexible needles, melts at 323° (corr.), and distils in small quantities almost without decomposition; it is slightly soluble in hot water, almost insoluble in ether or in concentrated hydrochloric acid, but dissolves easily in concentrated sulphuric acid at 100° without undergoing any change. The alkali salts crystallise in needles, and are easily soluble in hot water, but only slightly so in alkalis. The ammonium salt crystallises in pointed prisms or plates. Phenylxydichloropurine dissolves in considerable quantities in cold hydriodic acid of sp. gr. 1.96, and on warming, with or without the addition of phosphonium iodide, a compound which contains iodine and is easily soluble in alkalis, separates out.

3-Phenyl-1 : 4 : 6-trimethyluric acid,  $\begin{array}{c} \text{NMe}\cdot\text{CO}\cdot\text{C}^{\text{H}}\cdot\text{NMe} \\ \text{CO}\cdot\text{NMe}\cdot\text{C}^{\text{H}}\cdot\text{NPh} \end{array} > \text{CO}$ , prepared by shaking an alkaline solution of phenyluric acid with methyl iodide at 85°, crystallises in rhomb-like plates, melts at 265—266° (corr.), distils with slight decomposition at a higher temperature, is

soluble in about 30 parts of boiling alcohol, and is not attacked by cold alkalis, but dissolves on boiling, being decomposed in a similar manner to tetramethyluric acid.

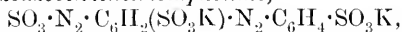
The aminophenols also act on phenyl cyanate in alkaline solution. The *phenyl carbamate* of *p*-hydroxydiphenylcarbamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , prepared from *p*-aminophenol, crystallises from about 100 parts of glacial acetic acid; it sinters at  $220^\circ$ , melts and decomposes at  $240^\circ$ , and is dissolved by prolonged boiling with alkali, being partially converted into *p*-hydroxydiphenylcarbamide,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , which is precipitated from the alkaline solution by acids, and separates from glacial acetic acid in spherical aggregates of needles, melts at  $221^\circ$  (corr.), is slightly soluble in hot water, ether, or benzene, and closely resembles Leuckart's isomeric ortho-compound.

E. W. W.

**Aminoazobenzenetrisulphonic Acid.** By ALFRED JUNGHAIN and MAX NEUMANN (*Ber.*, 1900, 33, 1366—1371).—4'-Aminoazobenzene-4 : 3' : 5'-trisulphonic acid,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})_2\cdot\text{NH}_2$ , is formed when aminoazobenzene hydrochloride is brought rapidly into fuming sulphuric acid and the mixture heated; it is much more readily soluble than the disulphonic acid, which is also formed, whilst its *potassium* salt is less soluble than that of the disulphonic acid. The acid is also formed by the sulphonation of the disulphonic acid, and crystallises in small plates, which have a silvery lustre; on reduction, it yields sulphanilic acid and a *p*-phenylenediaminedisulphonic acid,  $\text{C}_6\text{H}_2(\text{NH}_2)_2(\text{SO}_3\text{H})_2$  [ $\text{NH}_2:\text{NH}_2:\text{SO}_3\text{H}:\text{SO}_3\text{H} = 1:4:2:6$ ], which crystallises in white plates. Nitric acid converts this compound into picric acid, its constitution, and that of the trisulphonic acid, being thus proved.

The *dipotassium hydrogen* salt of aminoazobenzenetrisulphonic acid is precipitated when the normal salt is treated with hydrochloric acid, and crystallises in large, dark blue plates. The normal *barium* salt crystallises in yellow needles, and the *barium hydrogen* salt in steel, blue plates, whilst the *normal ammonium* salt crystallises in yellow plates.

*Potassium diazoazobenzenetrisulphonate*,



is formed when the normal *potassium* salt of the trisulphonic acid is diazotised, and crystallises in brown needles which decompose in the air; when boiled with alcohol, nitrogen is evolved, and *potassium hydrogen azobenzenetrisulphonate* is produced, which, however, could not be obtained pure. The trisulphonic acid itself dyes silk and wool a fast yellow; the azo-dyes formed with phenol,  $\beta$ -naphthol, and *p*-tolyl- $\beta$ -naphthylamine are very similar to those derived from aniline-yellow, but the shades are more yellowish or brownish.

A. H.

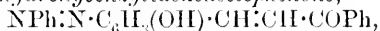
**Constitution of Hydroxyazo-compounds.** By KARL AUWERS [and G. MANN] (*Ber.*, 1900, 33, 1302—1315. Compare Abstr., 1897, i, 40).—The results of a cryoscopic examination of phenylhydrazones in *p*-dibromobenzene are tabulated. From these it is possible to formulate rules to decide from the cryoscopic behaviour of *p*-hydroxyazo-compounds in the same solvent whether they are quinone-hydrazones or



phenols. The determinations clearly show that they are phenols. This result is not in accordance with Hantzsch's views (*Abstr.*, 1899, i, 400), but agrees with the chemical behaviour of these substances (compare Hewitt, *Trans.*, 1900, 77, 99 and 712). R. H. P.

**Benzeneazosalicylaldehyde.** By WALTHER BORSCHKE (*Ber.*, 1900, 33, 1325—1328).—Benzeneazosalicylaldehyde can readily be prepared from hydroxyazobenzene and chloroform. The compound with aniline crystallises in brown needles melting at 135—136°.

*3-Benzeneazoo-6-hydroxybenzylideneacetophenone*,



is formed by the action of benzeneazosalicylaldehyde on acetophenone and crystallises in orange-red nodules which melt and decompose at 187—188°. The sodium compound forms garnet-red plates, with a green lustre. The same substance is also formed, but in small quantity, by the reaction of *o*-hydroxybenzylideneacetophenone on diazobenzene chloride. A. H.

**Sulphur Derivatives from *p*-Aminophenol and Hydroxyazobenzene.** By CRISTOPH RIS (*Ber.*, 1900, 33, 796—799).—*p*-Aminophenol (4 mols.), hydroxyazobenzene (2 mols.), and sulphur (7 at.) are melted in a porcelain beaker and kept well-stirred at a temperature of 180—190°, when ammonia and aniline are evolved; the fused mass is boiled with dilute hydrochloric acid, when a black dye remains undissolved, and, on the addition of sodium acetate to the acid filtrate, a greenish-white precipitate is deposited. This contains both nitrogen and sulphur (N = 8.56, S = 26.37 per cent.); it rapidly darkens when dried, even at low temperatures, possesses both basic and acidic properties, and dissolves in alcohol to a pale yellowish-grey solution, which, however, on exposure to the air, gradually deposits a thick, black precipitate. When treated with reducing agents, much hydrogen sulphide is evolved, and a product very similar to the original substance is produced; oxidising agents, on the other hand, give rise to a heavy, black dye which dissolves in alkalis to a black solution. A black dye is also formed when the original compound is heated with a further quantity of sulphur.

*m*-Amino-*o*-cresol, or *p*-phenylenediamine, may be employed instead of *p*-aminophenol and other hydroxyazo-compounds in place of hydroxyazobenzene. *p*-Aminophenol itself, when heated with sulphur, gives rise to a substance which is deposited as a greyish-white precipitate on the addition of sodium acetate solution to the hydrochloric acid extract of the fused mass. On oxidation, it yields a purple-black precipitate, and its ammonium sulphide solution, on exposure to the air, assumes a clear blue colour. It contains nitrogen 8.25, and sulphur 23.69 per cent., and is not leucothionol. J. J. S.

**Digestion of Fibrin and Albumin by Papain.** By V. HARLAY (*J. Pharm.*, 1900, [vi], 11, 172—178. Compare *Abstr.*, 1899, i, 835).—Papain, in the form of the diluted latex of *Carica hastifolia*, rapidly digests fibrin at 45—50°, and the action is only slightly retarded by rendering the solution feebly alkaline by sodium hydrogen carbonate, although boiling, or the presence of 0.34 per cent. of hydrochloric acid

totally prevents it. The liquid from the digestion gives with *Russula delicata* a colour change of red to green, resembling that obtained similarly in the peptic digestion of fibrin (*loc. cit.*); the final green obtained in the former case, however, has a slightly bluer shade. Little tyrosine, if any, appears to be formed, so that the digestion of fibrin by papain is markedly different from that effected by pancreatic juice.

The papain digestion of albumin is very similar to that effected by pepsin, although *Russula delicata* produces with the former a dark green solution having a characteristic absorption band in the orange of the spectrum, whereas in the case of pepsin this is absent; the solution, moreover, is dichroic, appearing green in transmitted, red in reflected light. With solutions obtained by peptic digestion, however, the same absorption band is observed after reduction with zinc and hydrochloric acid.

W. A. D.

**Action of Heat on Papain.** By V. HARLAY (*J. Pharm.*, 1900, [vi], 11, 268—272).—The digestive action of papain on fibrin is not changed by heating the dry enzyme for 3 hours at 100°, but in aqueous solution heat rapidly destroys the ferment; at 82.5°, the destruction is complete in 30 minutes, whilst at lower temperatures it takes place more slowly.

W. A. D.

**Yeast Extract and Precipitating Agents.** By ROBERT ALBERT and EDUARD BUCHNER (*Ber.*, 1900, 33, 971—975. Compare this vol., i, 329).—When fresh yeast extract is poured into a mixture of alcohol and ether, a precipitate is obtained which after drying has not lost its fermenting properties. This precipitate is not completely soluble in water, but the turbid liquid obtained possesses strong fermenting properties which are, however, greatly diminished when it is filtered. The dried precipitate is more readily soluble in glycerol, and the solution, after filtration, ferments just as readily as before; when the glycerol solution is poured into alcohol and ether, a precipitate is obtained which is also capable of inducing fermentation. It has been shown by experiment that yeast extract which has been allowed to remain in contact with 10 per cent. glycerol for some 20 hours at the ordinary temperature ferments more readily than the same extract which has been kept for the same length of time without the addition of glycerol. This is probably due to the fact that the addition of glycerol hinders, to a certain extent, the action of proteolytic enzymes in the extract which tend to destroy the zymase.

J. J. S.

## Organic Chemistry.

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**Configuration of Saturated Fatty Compounds.** By PAVEL IW. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1900, [ii], 61, 431—439).—The author opposes Krafft's view that in saturated fatty compounds the favoured configuration is the one which approximates to that of the corresponding polymethylene compounds. In the oxalic series, the dissociation constant steadily decreases as the molecular weight increases, suggesting that the two carboxyl groups are furthest apart and influence each other least in the higher homologues and do not tend to approach each other as they should do according to Krafft's hypothesis. In a number of other cases, it is pointed out that polymethylene compounds do not resemble the open-chain derivatives containing the same number of carbon atoms, but rather the corresponding dimethyl compounds; thus hexamethyleneamine resembles isopropylamine rather than the higher homologues, and ketopentamethylene and other cyclo-ketones resemble acetone in forming compounds with sodium hydrogen sulphite. T. M. L.

**Hydrogenation of Acetylene in Presence of Copper.** By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1900, 130, 1559—1561. Compare Abstr., 1899, i, 555).—When a mixture of acetylene and hydrogen, containing excess of the latter, is passed over finely-divided reduced copper at 200°, the resultant gas contains about 3 per cent. of olefines and 18 per cent. of ethane; with more compact copper at 170°, the percentage of olefine is increased nine-fold, whilst that of ethane is diminished by one-third. When the mixture contains half its volume of acetylene, the reaction sets in at 150°, and is attended by the formation of cuprene (this vol., i, 197); the yield of ethylene and its higher homologues is even greater than in the preceding experiments, whilst that of ethane falls to 2 per cent. G. T. M.

**Addition of Hypochlorous and Hypobromous Acids to Acetylene and to its Mono-substituted Derivatives.** By NICOLAUS M. WITTORFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 88—117).—The action of hypobromous acid on acetylene yields a small quantity of dibromoacetic acid, the chief product, however, being dibromoacetaldehyde, of which a new hydrate,  $C_2H_2OBr_2 \cdot 2H_2O$ , melting at 40—60°, was obtained. The action of hydroxylamine on this compound gives rise to glyoxime.

With allylene, hypobromous acid yields unsymmetrical dibromoacetone, which, by the action of hydroxylamine, is converted into methylglyoxime.

Trimethylallylene,  $CH_3C \cdot CMe_3$ , and hypobromous acid react together with the formation of a dibromopinacolin identical with the compound obtained by Scholl and Weil (*Chem. Zeit.*, 1899, 23, 189) by the action of bromine on pinacolin, and by Kondakoff (Abstr., 1899, i, 859) by treating pinacone with concentrated hydrobromic acid; the latter regarded it as having the constitution  $CH_2Br \cdot CO \cdot CMe_2 \cdot CH_2Br$ . The

authors find, however, that when heated in alcoholic solution with hydroxylamine hydrochloride and potassium hydroxide, it is converted into a dioxime,  $C_6H_{12}O_2N_2$ ; also when heated with 10 per cent. potassium hydroxide solution it yields trimethylactic acid,  $CMe_3 \cdot CH(OH) \cdot CO_2H$ . The compound must hence be *α*-dibromopinacolin,  $CMe_3 \cdot CO \cdot CHBr_2$ , the dioxime formed from it having the constitution  $CMe_3 \cdot C(:NOH) \cdot CH:NOH$ ; the latter crystallises from dilute alcohol in oblique prisms melting at  $101-102^\circ$ .

Hypobromous acid combines with phenylacetylene, giving dibromoacetophenone,  $CHBr_2 \cdot CPh$ , and a small quantity of a bromide probably identical with the compound obtained by Schramm (Abstr., 1885, 518) by brominating ethylbenzene in sunlight, to which the constitution  $CMePhBr_2$  was assigned. When treated with hydroxylamine, dibromoacetophenone yields phenylglyoxime.

Hypochlorous acid acts on acetylene and its mono-substituted derivatives in a manner analogous to that of hypobromous acid, the dichloroketones obtained yielding with hydroxylamine the same dioximes as the corresponding dibromo-compounds. Thus, with acetylene, the initial product of the reaction, which must be carried out at a low temperature and in presence of excess of hypochlorous acid, is dichloroacetaldehyde, most of which, however, undergoes oxidation to dichloroacetic acid. With allylene, *as*-dichloroacetone and a small quantity of methylglyoxal are formed. Trimethylallylene gives rise to the *α*-dichloropinacolin,  $CMe_3 \cdot CO \cdot CHCl_2$ , obtained by Fittig by the direct chlorination of pinacolin; with 10 per cent. potassium hydroxide solution, this compound yields trimethylactic acid. With phenylacetylene, hypochlorous acid gives *α*-dichloroacetophenone,  $CHCl_2 \cdot CPh$ , melting at  $20-21.5^\circ$ .

T. H. P.

**Hydrocarbon  $C_6H_{10}$  from Dimethylallylcarbinol.** By EUGÈNE LUBARSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 140-149).—The author has investigated the hydrocarbon  $C_6H_{10}$  obtained by Saytzeff (this Journal, 1877, ii, 298). It is prepared by treating dimethylallylcarbinol with hydrogen chloride in the cold, the chloride thus obtained being treated with alcoholic potash to remove hydrogen chloride. On fractionating the product in an atmosphere of carbon dioxide, the hydrocarbon is obtained as a colourless, mobile liquid boiling at  $73-76^\circ$ ; it has a characteristic hydrocarbon odour recalling that of kerosene, and shows slight violet-blue fluorescence. It has a sp. gr. 0.71427 at  $20^\circ/0^\circ$ ; 0.71504 at  $20^\circ/20^\circ$ ; 0.71415 at  $20^\circ/4^\circ$ . At  $20^\circ$ , it has the refractive indices  $\mu_a$  1.43840,  $\mu_\beta$  1.45450, the value for infinite wave-length being hence 1.41888; the molecular refraction (Perkin's formula) for the ray of infinite wave-length is 48.09, the value calculated from the composition of the hydrocarbon, and allowing for the presence of two double bonds, being 42.06; this difference is probably due to oxidation of the compound, as it absorbs oxygen readily from the air, giving a thick, slightly sticky, yellowish oil. On treating the hydrocarbon with hypochlorous acid, and acting on the additive compound thus obtained with an ethereal solution of potassium hydroxide, hydrogen chloride is removed and a compound formed having the composition  $C_6H_{10}O(OH)_2$ , and the probable constitution

$\text{CH}_2 \begin{matrix} \text{CMe(OH)·CH}_2 \\ \text{CH(OH)—CH}_2 \end{matrix} \text{O}$ . The hydrocarbon  $\text{C}_6\text{H}_{10}$  is hence probably *aa* methylallylethylene,  $\text{CH}_2\text{:CH·CH}_2\text{·CMe·CH}_2$ . T. H. P.

**Action of Zinc Dust on Trimethylene Bromide.** By ALESEI A. WOLKOFF and BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 118—139. Compare Abstr., 1899, i, 196).—The results obtained by Gustavson (Abstr., 1899, i, 421) and Tanatar (Abstr., 1899, i, 422) are criticised, and further experiments described, which lead to the following conclusions. Pure trimethylene cannot be obtained by the action of zinc dust and water on trimethylene bromide, or by the action of sodium on a xylene solution of trimethylene bromide; in both cases, the gas formed contains propane, and possibly hydrogen. The occurrence of propylene in the gas obtained by the action of zinc dust and alcohol on trimethylene bromide is due to the presence in the zinc dust of zinc oxide, which gives rise to ethyl  $\alpha$ -bromopropyl ether (*loc. cit.*), the latter being reduced by alcohol and zinc dust to propylene. The propane present is formed by the reduction of propyl bromide, itself formed by incomplete reduction of the trimethylene bromide. The action of bromine on the gas obtained from zinc dust and alcoholic solution of trimethylene bromide is as follows. The propane gives propyl or isopropyl bromide, which, by the further action of bromine, is almost completely converted into propylene bromide; the latter product is also formed from the propylene, whilst the trimethylene gives trimethylene bromide. Absorption by bromine cannot be used as a means of obtaining pure trimethylene, since, although the propylene is very quickly absorbed, the propane is taken up less quickly than is the trimethylene. T. H. P.

**Glycol Monoiodohydrin.** By ERNEST CHARON and PAIX-SÉAILLES (*Compt. rend.*, 1900, 130, 1407—1410).—When glycol monoiodohydrin is treated with aqueous potash, it yields ethylene oxide and a resinous product resembling aldol resin, but when gently heated with dry lead hydroxide, it yields acetaldehyde and lead iodide almost quantitatively.

In Buttleroff and Ossokin's experiments on the action of zinc methyl on the iodohydrin (*Annalen*, 1873, 165, 257), it is probable that vinyl alcohol was first formed, and changed at once into acetaldehyde, which, with the excess of zinc methyl, produced an alcohol that was in reality secondary, and not primary, as those observers supposed. In Meyer and Demuth's experiments with silver nitrite (*ibid.*, 1890, 256, 29), there was simple substitution, and the acetic acid observed by Henry was probably the result of a secondary action.

With ammonia, aniline, phenylhydrazine, and hydroxylamine, the iodohydrin yields the iodides of complex bases, which are being investigated.

The iodohydrin loses the elements of the halogen acid much more readily than chlorohydrin; the latter has no action on lead hydroxide.

C. H. B.

**Partial Synthesis of Erythritol.** By LÉON MAQUENNE (*Compt. rend.*, 1900, 130, 1402—1404).—*Acetylpylonic nitrile*, which forms white or yellowish plates melting at  $81.5^\circ$ , is obtained by

the action of acetic anhydride and sodium acetate on the seemingly non-crystallisable xyloseoxime prepared by the action of hydroxylamine on xylose. *l-Erythroseacetamide* is obtained from this nitrile by simply dissolving in a large excess of ammonia solution, and crystallises in colourless prisms which melt at  $166^{\circ}$  and are very soluble in cold water, although non-deliquescent. In order to obtain *l-erythritol*, the acetamide is hydrolysed, the erythrose reduced with sodium amalgam, and the erythritol separated in the form of benzoic acetal, from which it is isolated by hydrolysis. *l-Erythritol* crystallises from alcohol in slender, brilliant needles, and from water in bulky prisms, which melt at  $88^{\circ}$ ; its rotatory power in a 6 per cent. aqueous solution is  $[\alpha]_D + 4.3^{\circ}$ , but in a 1.5 per cent. alcoholic solution  $[\alpha]_D - 15^{\circ}$ . Its molecular weight, determined by the cryometric method, is 121, and, except for the sign of the rotation, it is identical with the product obtained by Bertrand by the hydrogenation of erythrulose or erythroketoze (this vol., i, 377).  
C. H. B.

**Reduction of Erythrulose and Preparation of a New Erythritol; *d*-Erythritol.** By GABRIEL BERTRAND (*Compt. rend.*, 1900, 130, 1472—1475. Compare this vol., i, 377).—*d-Erythritol* is obtained, together with the inactive modification, by reducing an acid solution of erythrulose with sodium amalgam. A crystal of the inactive compound is added to the syrupy product of reduction in order to induce the crystallisation of this modification, the mother liquor being then treated with benzaldehyde, and the *d-erythritol* isolated in the form of its benzylidene compound; the latter is hydrolysed with dilute sulphuric acid, the regenerated erythritol allowed to solidify, and then recrystallised from alcohol. It crystallises from water in rhombohedral prisms, melts at  $88-89^{\circ}$ , and has  $[\alpha]_D - 4.46^{\circ}$ . This substance is the optical antipode of the *l-erythritol* recently obtained by Maquenne from *l*-xylose (preceding abstract), and since it is derived from erythrulose it follows that this sugar is also a member of the *d*-series.  
G. T. M.

**Behaviour of Uranyl Acetate and some of its Double Salts towards Water.** By JOSEF ZEHENTER (*Monatsh.*, 1900, 21, 235—255).—Uranyl acetate,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , loses its water of crystallisation at  $110^{\circ}$ , and decomposes at  $275^{\circ}$ , leaving a residue of uranium trioxide (compare Wertheim, *J. pr. Chem.*, 1843, 29, 207). It has a sp. gr. 2.893 at  $15^{\circ}$  in benzene, and at the same temperature 7.694 parts dissolve in 100 parts of water. An aqueous solution remains unchanged in subdued light, but direct sunlight causes the separation of an unstable violet hydroxide (compare Zimmermann, *Annalen*, 216, 10, and Ebelmen, *J. pr. Chem.*, 1842, 27, 385). From a saturated solution of uranyl acetate, kept in twilight and constantly shaken, a *basic acetate*,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{UO}_2(\text{OH})_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , slowly separates, which is soluble in acids, insoluble in alcohol, and is coloured dark yellow by potash solution. A second *basic acetate*,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{UO}_2(\text{OH})_2$ , soluble in acids, is obtained as a sulphur-yellow powder when aqueous solutions are heated.

Potassium uranyl acetate,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{K}_2\text{C}_2\text{H}_3\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  (compare Wertheim, *loc. cit.*, and Rammelsberg, *Sitzb. preuss. Akad. Wiss.*, 1884,

2, 857), has a sp. gr. 2.396 at 15° in benzene. In 1 per cent. solution, it is not affected by light, but when heated, potassium hexauranate,  $K_2O_3 \cdot 6UO_3 \cdot 10H_2O$ , separates as a yellow powder soluble in acids, insoluble in potash and organic solvents, which loses  $5H_2O$  at 110°, and is decomposed above 300° with formation of uranosouranic oxide (compare Drenckman, *Zeit. gesamt. naturwiss.*, 17, 149). The *tetra-uranate*,  $K_2O_3 \cdot 4UO_3 \cdot 5H_2O$ , is obtained directly by repeatedly evaporating a solution of potassium uranyl acetate on the water-bath until no longer acid. Sodium uranyl acetate, when heated in aqueous solution in a reflux apparatus, yields uranyl hydroxide (compare Zimmermann, *Abstr.*, 1886, 598); when evaporated on the water-bath, *sodium pentauranate*,  $Na_2O_3 \cdot 5UO_3 \cdot 5H_2O$ , is produced. Ammonium uranyl acetate has a sp. gr. 2.219 at 15° in benzene, and in aqueous solution decomposes after a short time (compare Wertheim, *loc. cit.*), or at once on heating or evaporation, forming a *hexauranate*,  $(NH_4)_2U_6O_{19} \cdot 10H_2O$ , which, when heated, yields ammonia and uranosouranic oxide.

R. L. J.

**Methods for the Preparation of Acrylic Acid.** By EINAR BILMANN and ALFRED WÖHLK (*J. pr. Chem.*, 1900, [ii], 61, 199).—An enumeration of the various available methods for the preparation of acrylic acid.

R. H. P.

**Acrylic Acid from Glycerol.** By ALFRED WÖHLK (*J. pr. Chem.*, 1900, [ii], 61, 200—214).—The various methods of preparing acrylic acid from glycerol have been reinvestigated, and are fully described.

R. H. P.

**Preparation of Acrylic Acid from Allyl Alcohol.** By EINAR BILMANN (*J. pr. Chem.*, 1900, [ii], 61, 215—224).—A detailed description of the preparation of acrylic acid from allyl alcohol by means of  $\alpha\beta$  dibromopropyl alcohol and  $\alpha\beta$ -dibromopropionic acid.

*Manganese* acrylate and *copper* acrylate,  $2(C_3H_3 \cdot CO_2)_2Cu \cdot H_2O$ , are both soluble salts. The *mercuric* acrylate,  $HgO \cdot (C_3H_3 \cdot CO_2)_2Hg$ , is precipitated by alcohol from a solution of mercuric oxide in dilute acrylic acid solution.

R. H. P.

**$\gamma$  Chlorocrotonic Acid.** By ROBERT LESPIEAU (*Compt. rend.*, 1900, 130, 1410—1411).— $\gamma$ -Chlorocrotononitrile,  $CH_2Cl \cdot CH : CH \cdot CN$ , obtained by the action of phosphoric oxide on the nitrile formed by the action of hydrocyanic acid on epichlorhydrin is a colourless liquid of sp. gr. 1.1495 at 0°, which boils at 73—73.5° under 15 mm. pressure, and strongly attacks the skin. *Ethyl  $\gamma$ -chlorocrotonate*, obtained similarly from the ethyl salt formed when the same nitrile is hydrolysed in presence of alcohol, boils at 191—193° under 750 mm. pressure.  $\gamma$ -Chlorocrotonic acid,  $CH_2Cl \cdot CH : CH \cdot CO_2H$ , is a white solid with a strong odour; it melts at 76.5—77.5°, and distils in a vacuum without decomposing. It is prepared by the action of dilute alcoholic potash on the ethyl salt, and cannot be obtained by hydrolysis of the nitrile. When the latter is treated with potassium hydroxide, it loses chlorine, and when treated with hydrochloric acid it yields the dichlorobutyric acid,  $CH_2Cl \cdot CHCl \cdot CH_2 \cdot CO_2H$ , which melts at 45—50°. C. H. B.

**Action of Hydrogen Bromide on Ricinoleic Acid and on its Acetyl Derivative.** By ALEXANDER KASANSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 149—155).—The action of hydrogen bromide in the cold on ricinoleic acid gives first a monobromo-acid of the composition  $C_{18}H_{33}O_2Br$ , and if the action be continued, a dibromostearic acid,  $C_{18}H_{31}O_2Br_2$ , is obtained; on reduction, both of these bromo-acids yield stearic acid. Both Krafft's (Abstr., 1888, 1270) and Goldsobel's (Abstr., 1895, i, 81) formulæ for ricinoleic acid point to the possibility of converting it, by the action of hydrogen bromide, into two isomeric dibromostearic acids; on reduction, however, those derived from Krafft's formula would give two different acids, whilst the two dibromo-acids indicated by Goldsobel's constitution for ricinoleic acid would yield one and the same product—stearic acid. The latter formula is hence supported by the author's results. On acetylating ricinoleic acid and passing hydrogen bromide into an acetic acid solution of the acetyl compound, a bromoacetyl derivative of the composition  $C_{18}H_{31}O_2Br \cdot OAc$  is obtained. On reduction, this yields a *hydroxy-stearic acid*,  $C_{18}H_{35}O_2 \cdot OH$ , melting at  $81-82^\circ$ , and re-solidifying at  $78.5-78^\circ$ , but differing from the ordinary acid of this composition obtained from oleic or elaidic acid in its solubility in alcohol and ether; 100 parts of a 99.5 per cent. alcoholic solution saturated at  $20.5^\circ$  contain 13.24 parts of the acid, the number for an ethereal solution at  $18.5^\circ$  being 5.39.

T. H. P.

**Behaviour of Dibasic  $\beta$ -Hydroxy-acids on Boiling with Aqueous Sodium Hydroxide.** By FRITZ FICHTER and CAMILLE DREYFUS (*Ber.*, 1900, 33, 1452—1455).—Dibasic  $\beta$  hydroxy-acids, when boiled with 20 per cent. aqueous sodium hydroxide for 24 hours, lose water and yield unsaturated dicarboxylic acids. Thus,  $\beta$ -hydroxyglutaric acid yields 50 per cent. of glutaconic acid, and malic acid 60 per cent. of pure fumaric acid. *iso* Butylparaconic acid yields 13 per cent. of *isobutylitaconic acid*, whilst phenylparaconic acid gives a mixture of 26 per cent. of phenylitaconic acid and 40 per cent. of phenylisoparaconic acid (m. p.  $168^\circ$ , Fittig, this vol., i, 397); from  $\delta$ -caprolactone- $\gamma$ -carboxylic acid (Abstr., 1897, i, 13), a 14 per cent. yield of  $\alpha$ -ethylideneglutaric acid (Fichter and Eggert, Abstr., 1898, i, 630) is obtained.

W. A. D.

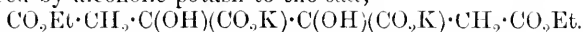
**Action of Cyanogen Chloride on Ethyl Acetonedicarboxylate.** By JUVÉNAL DÉRÔME (*Compt. rend.*, 1900, 130, 1475—1478).—The sodium derivative of ethyl cyanoacetonedicarboxylate is produced by treating ethyl acetonedicarboxylate successively with sodium ethoxide and cyanogen chloride.

*Ethyl cyanoacetonedicarboxylate*, obtained by the action of dilute acids on the preceding substance, is crystalline, melts at  $43-44^\circ$ , and is soluble in the ordinary organic solvents. This compound behaves as a monobasic acid, and yields *silver*, *copper*, and *barium* derivatives having the formulæ  $C_{10}H_{12}O_5Na$ ,  $(C_{10}H_{12}O_5N)_2Cu$ , and  $(C_{10}H_{12}O_5N)_2Ba$ . The *ethyl* derivative,  $C_{10}H_{12}O_5N \cdot Et$ , obtained by the action of ethyl iodide on the silver compound, separates from an ethereal solution in colourless, silky crystals melting at  $55^\circ$ ; this substance may have either a ketonic or an enolic constitution.

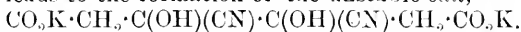
G. T. M.



**Action of Hydrocyanic Acid on Ethyl Cetipate.** By RENÉ THOMAS-MAMERT and ST. WEIL (*Bull. Soc. Chim.*, 1900, [iii], 23, 430—437).—Hydrocyanic acid itself has little or no action on ethyl cetipate (oxalldiacetate), but the gradual addition of hydrochloric acid to a mixture of potassium cyanide with an ethereal solution of the ester results in the formation of about 3 per cent. of *ethyl βγ-dihydroxy-βγ-dicyanohexanedioate*,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CN})\cdot\text{C}(\text{OH})(\text{CN})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which crystallises in large, white tablets melting at  $164^\circ$ , and is hydrolysed by alcoholic potash to the *salt*,



On the other hand, the action of potassium cyanide on oxalldiacetic acid itself, leads to the formation of the unstable *salt*,



The chief product, however, of the first reaction is a pale yellow, crystalline *substance* of the composition  $\text{C}_{21}\text{H}_{25}\text{O}_{12}\text{K}$ , which is probably formed by the condensation of 2 mols. of ethyl cetipate with subsequent fixation of hydrogen cyanide and hydrolysis of the compound thus formed. The corresponding *acid*,  $\text{C}_{21}\text{H}_{26}\text{O}_{12}$ , was obtained as a green, uncrystallisable oil.

The difficulty with which ethyl cetipate reacts with hydrogen cyanide suggested that the ester might have the enolic formula,  $\text{CO}_2\text{Et}\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , but an examination of its behaviour towards benzylideneaniline (compare Schiff, *Abstr.*, 1898, i, 237), made with a view to deciding this question, gave no definite results. Experiments with benzylidene-β-naphthylamine were also indecisive, the product of the action of this compound on ethyl cetipate being a white, crystalline *substance*,  $\text{C}_{41}\text{H}_{40}\text{N}_2\text{O}_8$ , melting at  $125^\circ$ , whilst in the presence of a trace of piperidine a red, crystalline *substance* melting at  $80^\circ$  is obtained, which appears to have the composition  $\text{C}_{38}\text{H}_{35}\text{O}_{11}\text{N}_4$ , and to be a condensation product, and not an isomeride, of the compound formed in the absence of piperidine. It is also noteworthy that no definite reduction products could be obtained from ethyl cetipate, however the conditions were varied. N. L.

**Compounds of Bromal with Formaldehyde.** By ADOLF PINNER (*Ber.*, 1900, 33, 1432—1433).—Of several aldehydes examined, only bromal has been found to react with formaldehyde in the same way as chloral does (*Abstr.*, 1898, i, 626). About half the quantity of sulphuric acid used in the latter case was employed, and the mixture was allowed to remain for weeks; the solid product was separated by extraction with boiling alcohol into the sparingly soluble *hexabromodimethyltetroxan*, which melts far above  $250^\circ$ , and the soluble *hexabromodimethyltrioxin*, which melts and decomposes at  $212\text{--}213^\circ$ .

The resinous product, formerly supposed to be dichloral methylene-glycoloxide, was really an impure tetroxin. C. F. B.

**Action of Bromine on Polymeric Aldehydes. I.** By ADOLF FRANKE (*Monatsh.*, 1900, 21, 205—209).—Under certain conditions, paraldehydes yield derivatives without previous change to the monomeric state. Para-*α*-bromoisobutaldehyde (trimeric), obtained in almost theoretical quantity by adding bromine to a solution of para-isobutaldehyde in carbon disulphide cooled to  $-15^\circ$ , crystallises from dilute

alcohol in glistening, white needles and melts at  $129^{\circ}$  (compare Lipp, *Annalen*, 1882, 211, 352), and is soluble in ether, light petroleum, benzene, acetone, or hot alcohol. It is scarcely attacked when heated with acids, alkalis, or acid dichromate solution, and metallic sodium, methylic iodide, or zinc ethyl fail to remove bromine. By continued heating at  $150^{\circ}$ , it is readily converted into the monomeric condition.

R. L. J.

**2-Methyl-2-Bromopropenal [ $\alpha$ -Bromo*isobutaldehyde*].** By ADOLF FRANKE (*Monatsh.*, 1900, 21, 210—215).—This substance, prepared by heating parabromo*isobutaldehyde* (see preceding abstract), distils in an atmosphere of carbon dioxide at  $113^{\circ}$  under 750 mm. pressure as a clear, mobile liquid of sp. gr. 1.555, which fumes in moist air and violently attacks the mucous membrane. If pure, and kept in a closed flask, it remains unaltered for weeks, but a trace of acid or moisture causes polymerisation. Acid dichromate solution removes bromine and forms  $\alpha$ -hydroxy*isobutyric acid*; similarly, when heated with water,  $\alpha$ -hydroxybutaldehyde is produced, which was not observed to polymerise when kept, as stated by Gorboff and Kessler (*Abstr.*, 1888, 814).  $\alpha$ -Bromo*isobutaldehyde* reacts with hydroxylamine to form  $\alpha$ -hydroxybutaldoxime, a thick, colourless, soluble liquid which distils at  $110^{\circ}$  under 19 mm. pressure. By the action of acetic anhydride, this oxime yields a dark, resinous oil, which is destroyed by distillation and decomposed by sodium carbonate into acetone and hydrogen cyanide.

R. L. J.

**An Aldol from *iso*-Butaldehyde and Formaldehyde.** By LEO WESSELY (*Monatsh.*, 1900, 21, 216—234).—By the action of potassium carbonate instead of alcoholic potash or calcium hydroxide (compare Just, *Abstr.*, 1896, i, 413; and Apel and Tollens, *Abstr.*, 1894, i, 353) on a mixture of *isobutaldehyde* and formaldehyde, an aldol is obtained which distils at  $67$ — $69^{\circ}$  under 14 mm. pressure, and melts at  $89$ — $90^{\circ}$ . It dissolves with some difficulty in many organic solvents, is oxidised by bromine water or permanganate, but not attacked by atmospheric oxygen even when left for a long time in aqueous solution. Under 747 mm. pressure, two-thirds distil over at  $172$ — $173^{\circ}$  unchanged, the remaining third being decomposed into the aldehydes. The molecular weight, as determined by cryoscopic and ebullioscopic methods, indicates a dimeric aldol; by continued heating (as in a vapour density determination), it becomes monomeric, and the derivatives appear to be of the latter type. By reduction, Just's pentaglycol (*loc. cit.*) is obtained, and by oxidation with potassium permanganate, dimethylmalonic acid, together with the fourth of the five theoretically possible hydroxyvaleric acids.

The latter, which the author names *hydroxypivalic acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , crystallises in the rhombic system, melts at  $123^{\circ}$ , dissolves sparingly in ether, and when oxidised yields dimethylmalonic acid, which melts at  $185^{\circ}$ , not at  $117^{\circ}$ , as stated in Beilstein's handbook.

The aldol forms a triacetyl derivative,  $\text{C}_{11}\text{H}_{18}\text{O}_6$ , of mol. weight 246, which distils at  $136$ — $137^{\circ}$  under 12 mm. pressure, and an oxime,  $\text{C}_7\text{H}_{11}\text{O}_2\text{N}$ , which boils at  $129^{\circ}$  under 18 mm. pressure, melts at  $29.5^{\circ}$ ,

and has a molecular weight of 234 or 117, according to the temperature of estimation.

R. L. J.

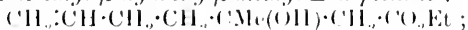
**The Negative Nature of Unsaturated Groups of Atoms.** By FERDINAND HENRICH (*Ber.*, 1900, 33, 1435—1438).—The author (*Abstr.*, 1899, i, 469, &c.) has published the view that all unsaturated groups of atoms exert a certain negative action, rendering replaceable the hydrogen atoms of an adjacent  $\text{CH}_2$  group. Modern opinion inclines to the view that such substitution does not take place directly in the  $\text{CH}_2$  group of the ketonic form, but that the latter first undergoes a transformation into the tautomeric enolic form. The author points out that the two views are not incompatible, as Hantzsch and Kissel (this vol., i, 89) seem to think.

C. F. B.

**Allylacetone.** By JULIUS VON BRAUN and FRITZ STECHELE (*Ber.*, 1900, 33, 1472—1477).—Allylacetone prepared by Conrad's method (*Annalen*, 1878, 192, 153) and purified by means of the *semicarbazone* (m. p. 100—102°), boils at 129.5° and has a sp. gr. 0.8430; on oxidation with sodium hypobromite, it yields bromoform and allylacetic acid, whilst with 1 per cent. aqueous potassium permanganate, it gives rise to formaldehyde and lævulic acid; attempts to bring about, by means of acids and alkalis, a rearrangement of allylacetone to either methyl  $\alpha$ -ethylideneethyl ketone,  $\text{CHMe}:\text{CH}:\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ , or keto-hexamethylene failed; hydrogen bromide, either gaseous or dissolved in glacial acetic acid, is also without action on the ketone, methyl  $\alpha$ -bromobutyl ketone (Lipp, *Abstr.*, 1886, 218) not being formed. Attempts to obtain the foregoing methyl  $\alpha$ -ethylideneethyl ketone from propenyl bromide,  $\text{CHMe}:\text{CHBr}$ , and sodium dibromobutyrate were without issue. The *dibromide* of allylacetone is a colourless oil which decomposes when kept, and when treated with alkalis gives rise to complex decomposition products.

The *oxime* of allylacetone boils at 190°, and when reduced with sodium in ethyl alcohol yields apparently  $\epsilon$ -amino- $\Delta^a$ -hexylene ("butallylmethylcarbinamine," Merling, *Abstr.*, 1891, 1506); attempts to convert the dibromide of the latter into a pyrrolidine derivative by loss of hydrogen bromide (compare Merling, *loc. cit.*) gave no definite result. On the other hand, treatment of the foregoing oxime with phosphorus pentoxide (compare Wallach, this vol., i, 44) appears to yield dimethylpyrrolidine. When the oxime is reduced with sodium in boiling amyl alcohol, a small quantity only of  $\beta$ -aminoheptane, boiling at 116°, is obtained, owing to complex decomposition occurring; the base was isolated in the form of the *platinichloride*.

When allylacetone is treated with ethyl bromoacetate and zinc according to Reformatsky's method (*Abstr.*, 1887, 717), it gives a 65 per cent. yield of *ethyl  $\beta$ -hydroxy- $\beta$ -methyl- $\Delta^a$ -heptenoate*,

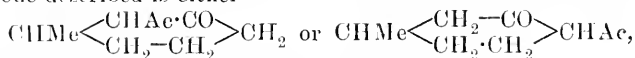


this boils at 123—125° under 20 mm. pressure, whilst the corresponding *acid*,  $\text{C}_8\text{H}_{14}\text{O}_3$ , is a colourless liquid boiling at 175° under 25 mm. pressure. On heating the latter for 6 hours with acetic anhydride containing sodium acetate, water is split off and  $\beta$ -methyl- $\alpha$ -heptadienoic acid,  $\text{CH}_2:\text{CH}:\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}\cdot\text{CO}_2\text{H}$ , formed; this boils at 138—140° under 18 mm. pressure, has a sp. gr. 0.9712 at

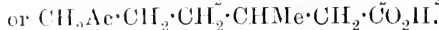
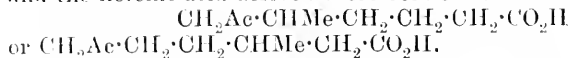
$19^\circ$ ,  $\mu_D = 1.4604$ , and yields a stable *silver* salt; with bromine in glacial acetic acid solution, it yields a *tetrabromide* as an oil, and on oxidation gives rise to formaldehyde and lævulic acid, facts which determine its structure.

W. A. D.

**Cyclic  $\beta$ -Diketones. I.** By GEORGES LESER (*Bull. Soc. Chim.*, 1900, [iii], 23, 370—374).—Three cyclic  $\beta$ -diketones, having one carbonyl group in the nucleus and the other in the side chain, have hitherto been described, two of these being obtained by Baeyer from menthone and tetrahydrocarvone, whilst the third, which differs from the other two in undergoing only partial hydrolysis and in not forming a copper salt, was prepared by the author (Abstr., 1899, i, 743) from acetyl-methylheptenone. In order to ascertain the cause of these differences in behaviour, a general method for the preparation of similar ketones was sought in the application of Claisen's reaction to cyclanones. Wallach's methylcyclohexanone, when treated with sodium and ethyl acetate, yields 25—30 per cent. of its weight of *acetylmethylcyclohexanone*, which was obtained as a colourless liquid boiling at  $122^\circ$  under 14 mm. pressure, and having a sp. gr. 1.030 at  $12^\circ$ ; it has all the characteristics of  $\beta$ -diketones, since it is soluble in cold alkalis, gives a red coloration with ferric chloride, forms a well crystallised sodium hydrogen sulphite derivative, and yields a dioxime which melts and decomposes at  $171$ — $172^\circ$ . When boiled with aqueous or alcoholic potash, it undergoes partial hydrolysis with the formation of a *ketonic acid*,  $C_9H_{16}O_3$ , which boils at  $172$ — $174^\circ$  under 8 mm. pressure, forms a semicarbazone melting at  $141$ — $142^\circ$ , and is converted by oxidation with sodium hypobromite in the cold into an acid which appears to be identical with  $\beta$ -methylpimelic acid. From these results, the conclusion is drawn that the acetylmethylcyclohexanone described is either



and the ketonic acid derived therefrom either



N. L.

**Double Thiocyanates and Cyanides.** By PAUL WALDEN (*Zeit. anorg. Chem.*, 1900, 23, 373—377).—The author has determined the electric conductivity of the following salts: potassium silver cyanide, potassium mercury cyanide, potassium zinc cyanide, potassium cadmium cyanide, sodium nitroferri-cyanide, potassium nickel cyanide, potassium platinum thiocyanate, potassium cobalt cyanide, and potassium manganese cyanide. The values for  $\Delta = (\mu_{1024} - \mu_{32})$  are in accordance with the view that these compounds are complex salts.

E. C. R.

**Action of Cyanogen Bromide on Tertiary Amines.** By JULIUS VON BRAUN (*Ber.*, 1900, 33, 1438—1452).—Cyanogen bromide reacts with tertiary amines,  $NR^1R^1R^{11}$ . In some cases, the transient formation of a solid substance, presumably a compound,  $NR^1R^1R^{11}Br \cdot CN$ , can be observed; in all cases, the final products are a cyanamide,  $NR^1R^{11} \cdot CN$ , and an alkyl bromide,  $R^1I$ . In the case of dimethylaniline,

and in this case only, the formation of a tetralkylammonium salt,  $\text{NMe}_3\text{PhBr}$ , was observed in amount equivalent approximately to 2 mols. per 3 of the cyanamide; without doubt, the alkyl bromide, formed as indicated above, had added itself on to some of the tertiary amine which had not yet reacted with the cyanogen bromide. In the case of tripropylamine, ethyldipropylamine, methyldipropylamine, and tribenzylamine, the hydrobromide of the amine was formed in addition to the cyanamide. It is always the smallest of the alkyl radicles that is eliminated as the alkyl bromide; this was distilled off, and then the cyanamide was distilled over under diminished pressure. The latter was identified by hydrolysing it with acid agents into the corresponding secondary amine,  $\text{NHR}^{11}\text{R}^{11}$ , or by converting it with alcoholic ammonia and hydrogen sulphide into the corresponding thiocarbamide,  $\text{NR}^{11}\text{R}^{11}\cdot\text{CS}\cdot\text{NH}_2$ .

Methyldipropylamine, ethyldipropylamine, and tripropylamine react very vigorously with cyanogen bromide; ether may be used as a diluent. Dimethylaniline, methylethylaniline, and diethylaniline react less readily, and the first somewhat abnormally, as just indicated. Methylpropylaniline, ethylpropylaniline, and dipropylaniline react still less readily. Diphenylamine does react, but the reaction has to be accelerated by heating for 2 hours at  $60\text{--}70^\circ$ ; the same is true of tribenzylamine. Diphenylmethylaniline and triphenylamine do not react at all with cyanogen bromide.

Most of the substances obtained seem to be known already. *Phenylpropylecyanamide* is, perhaps, new; it boils at  $140\text{--}142^\circ$  under 10 mm., and at  $281^\circ$  under atmospheric pressure, decomposing slightly in the latter case.

By treating a tertiary amine with cyanogen bromide and hydrolysing the resulting cyanamide, the smallest radicle of the amine can be eliminated and a secondary amine obtained. The method is a convenient one, and may prove useful in the investigation of alkaloids.

C. F. B.

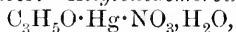
**Methylisocarbamide.** By JULIUS STIEGLITZ and RALPH H. MCKEE (*Ber.*, 1900, 33, 1517—1519. Compare this vol., i, 310).—A quantitative yield of methylisocarbamide hydrochloride is readily obtained by passing dry hydrogen chloride (1.08 mols.) into a solution of cyanamide (1 mol.) in methyl alcohol (25 mols.), allowing the solution to remain for 2 hours, and then distilling off the excess of alcohol at  $40^\circ$ . The base is a white, crystalline solid melting at  $44\text{--}45^\circ$ , and distilling at  $82^\circ$  under 9 mm. pressure; it has strong basic properties, and readily abstracts both moisture and carbon dioxide from the atmosphere. When heated with very dilute hydrochloric acid at  $100^\circ$  in sealed tubes, it yields methyl chloride and carbamide. The author considers that this affords an explanation of observations made by Gabriel (*Abstr.*, 1896, i, 121), and by Menne (this vol., i, 286).

*Ethylisocarbamide*,  $\text{NH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , melts at  $42^\circ$ , and distils at  $95\text{--}96^\circ$  under 15 mm. pressure.

J. J. S.

**Action of Allyl Alcohol and of Ethylene on Mercuric Salts.** By EINAR BILMANN (*Ber.*, 1900, 33, 1641—1655. Compare Hofmann and Sand, this vol., i, 384, 385, 386).—*Allyloxidemercuric sulphate*,

$(C_3H_5 \cdot O \cdot Hg)_2SO_4 \cdot 4H_2O$ , obtained as a crystalline precipitate when allyl alcohol is mixed with a solution of mercuric oxide in sulphuric acid and the mixture kept for 2—4 hours, is readily soluble in water and in ammonium or sodium hydroxide, and may be recrystallised from boiling water. When dissolved in 20 per cent. ammonium hydroxide and mixed with three times its volume of alcohol, it yields crystals of *allyloxidemercuric ammonium sulphate*,  $(C_3H_5 \cdot O \cdot Hg)_2(NH_3)_2SO_4$ , which are readily soluble in water. *Allyloxidemercuric nitrate*,



obtained by the action of allyl alcohol on an excess of mercuric nitrate, forms colourless crystals, and, unlike Hofmann and Sand's compound, is readily soluble in water, also in ammonia or potassium hydroxide, the latter solutions yielding a white precipitate on the addition of ammonium sulphide. If the preparation is not made in the cold, insoluble products are obtained. *Allyloxidemercurian ammonium nitrate*,  $C_3H_5 \cdot O \cdot Hg(NH_3) \cdot NO_3$ , forms colourless crystals readily soluble in water, and the solution has an alkaline reaction, and when boiled evolves ammonia. *Allyloxidemercuric acetate*,  $2C_3H_5O \cdot Hg \cdot C_2H_3O_2 \cdot H_2O$ , forms small, star-shaped, colourless crystals readily soluble in water; when recrystallised from hot water, it crystallises anhydrous in the form of short prisms. When solutions of the sulphate, nitrate, and acetate are treated with potassium bromide or chloride, *allyloxidemercuric bromide* and *chloride* are obtained as white precipitates. When precipitated mercuric oxide is shaken with allyl alcohol and water, an alkaline liquid is obtained which gives a precipitate with hydrobromic acid.

*Ethanolmercuric sulphate*,  $(OH \cdot CH_2 \cdot CH_2 \cdot Hg)_2SO_4$ , obtained by slowly bubbling ethylene through a solution of mercuric oxide in sulphuric acid for some hours, forms a colourless, crystalline precipitate sparingly soluble in cold water, but soluble in hot water, ammonia, or potassium hydroxide. *Ethanolmercuric bromide*,  $OH \cdot CH_2 \cdot CH_2 \cdot HgBr$ , is insoluble in water, but soluble in ammonia.

Various attempts to prepare Hofmann and Sand's allene compounds have been made, but without success.

The constitution of the allyl oxide compound is represented as  $CH_2 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CH \cdot HgX$ , as the alternative formula,  $\begin{smallmatrix} CH_2 \\ | \\ O \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} CH \cdot CH_2 \cdot HgX$ , contains an asymmetric carbon atom, and all attempts to resolve the compound into optically active constituents by the aid of *d*-tartaric acid have been unsuccessful. J. J. S.

**Iodoso-, Iodoxy-, and Iodonium Compounds derived from Iodo- and Chloriodo-mesitylene.** By CONRAD WILLGERODT and HEINRICH ROGGATZ (*J. pr. Chem.*, 1900, [ii], 61, 423—430).—*Iodoso-mesitylene*,  $C_6H_2Me_3 \cdot IO$ , a greyish-yellow, amorphous mass of characteristic odour, is only slightly soluble in most solvents and decomposes on keeping into iodomesitylene and iodoxy-mesitylene. The *chloride*,  $C_6H_2Me_3 \cdot ICl_2$ , crystallises in yellow needles, and rapidly changes into chloriodomesitylene. The *acetate*,  $C_6H_2Me_3 \cdot I(OAc)_2$ , crystallises from acetic acid in white needles, melts at  $158^\circ$ , and is fairly stable. The yellow *chromate* explodes before it is completely dry.

*Iodoxyesitylene*,  $C_6H_2Me_3 \cdot IO_2$ , prepared by warming iodosesitylene with chloroform, or alone, or in a current of steam, crystallises from acetic acid in white needles and explodes at  $195^\circ$ .

*Dimesityliodonium hydroxide*,  $I(C_6H_2Me_3)_2 \cdot OH$ , was prepared by grinding a molecular mixture of iodosesitylene and iodoxyesitylene with moist silver oxide. The *chloride* crystallises from alcohol in needles, melts at  $122^\circ$ , and is insoluble in water. The *bromide* crystallises from alcohol in yellow needles and melts at  $139^\circ$ . The *iodide* is an amorphous, yellow precipitate insoluble in water or ether, and melts at  $194^\circ$ . The *nitrate* melts at  $126^\circ$ . The *hydrogen sulphate*,  $I(C_6H_2Me_3)_2 \cdot HSO_4$ , crystallises in long, white flakes, and melts at  $167^\circ$ . The *chromate* is a yellow, amorphous precipitate, and decomposes at  $101^\circ$ . The *platinichloride*,  $[I(C_6H_2Me_3)_2]_2PtCl_6$ , is a yellow, amorphous powder which decomposes at  $151^\circ$ . The *mercurichloride*,  $[I(C_6H_2Me_3)_2Cl]_2HgCl_2$ , decomposes at  $130^\circ$ .

*Phenylmesityliodonium hydroxide*,  $C_6H_2Me_3 \cdot IPh \cdot OH$ , was prepared from iodoxybenzene and iodosesitylene. The *chloride* crystallises from alcohol and melts at  $94^\circ$ . The *mercurichloride* crystallises from hot water in white needles and decomposes at  $247^\circ$ . The *platinichloride* melts at  $173^\circ$ .

*Dichloroethylmesityliodonium chloride*,  $C_6H_2Me_3 \cdot ICl \cdot C_2H_3Cl_2$ , prepared by the action of mesityliodosochloride on a compound of silver acetylide and silver chloride suspended in water, crystallises in white flakes and melts at  $149^\circ$ . The *platinichloride* forms yellow needles and melts at  $133^\circ$ .

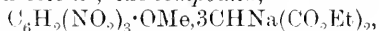
*Chloriodomesitylene*, prepared by the action of chlorine on iodosesitylene at the ordinary temperature, crystallises from chloroform in white needles, and melts at  $180^\circ$ . *Chloriodosomesitylene*,  $C_6HMe_3Cl \cdot IO$ , resembles iodosesitylene; the *chloride*,  $C_6HMe_3Cl \cdot ICl_2$ , crystallises from benzene in yellow needles, and readily decomposes into chloriodomesitylene, the chlorine being liberated instead of passing into the nucleus; the *acetate* crystallises from acetic acid in white needles and melts at  $169^\circ$ . *Chloriodoxyesitylene*,  $C_6HMe_3Cl \cdot IO_2$ , separates from acetic acid in an amorphous state and melts without exploding at  $222^\circ$ .

T. M. L.

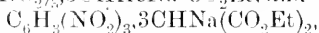
**Certain Coloured Substances derived from Nitro-compounds.** By C. LORING JACKSON and F. H. GAZZOLO (*Amer. Chem. J.*, 1900, 23, 376—396. Compare Abstr., 1899, i, 744).—The coloured substances resulting from the action of sodium alkyl oxides on certain nitro-compounds were considered by Meyer (*Ber.*, 1894, 27, 3156) to be formed by the replacement of a hydrogen atom of the benzene nucleus by the sodium atom, but this view was shown to be incorrect by Lobry de Bruyn (Abstr., 1895, i, 653). Hantzsch and Kissel (this vol., i, 89) regard them as additive compounds in which the sodium alkyl-oxide is added to the nitro-group, whereas the observations of the present authors are best explained on the hypothesis that the carbon of the benzene nucleus, as well as the nitro-group, is involved, and that the substances possess a quinonoid structure.

When a solution of trinitroanisole or trinitrobenzene in benzene is

treated with a solution of ethyl sodioacetoacetate or sodiomalonate in the same solvent, a red precipitate is produced which consists of a compound of 1 mol. of the nitro-compound with 3 mols. of the ethereal salt. These substances are amorphous powders, soluble in water, alcohol, or acetone; they explode on heating, and are instantly decomposed by acids. The compound,  $C_6H_2(NO_2)_3 \cdot OMe, 3CHAcNa \cdot CO_2Et$ , is of a deep crimson colour; the compound,



possess a deep maroon colour, and does not react with ethyl iodide. The compounds,  $C_6H_3(NO_2)_3, 3CHAcNa \cdot CO_2Et$ , and



are of a brownish-red and a rich maroon colour respectively; the latter is decomposed by bromine with formation of trinitrobenzene and sodium bromide.

The compound,  $C_6H_3(NO_2)_3, 3C_2H_5ONa$ , obtained by the action of sodium amylxide on trinitrobenzene, is a dark crimson, amorphous powder, soluble in water, alcohol, or acetone. Sodium methoxide and ethoxide yield similar products, whilst sodium phenoxide produces a red colour, but no precipitate. Coloured substances are also formed by the action of sodium hydroxide and benzyl cyanide on trinitrobenzene, but cannot be isolated. When picramide is treated with sodium methoxide, a brick-red precipitate is obtained, which rapidly decomposes. 2:4-Dinitrotoluene gives a very unstable, red precipitate both with sodium methoxide and with ethyl sodiomalonate. 2:4-Dinitro-*m*-xylene produces a coloration with sodium methoxide, but not with ethyl sodioacetoacetate or sodiomalonate; 2:4:6-trinitro-*m*-xylene yields an unstable red substance with each of these reagents, whilst dinitromesitylene, trinitromesitylene, and the triethyl ether of dinitrophenol give only negative results.

Similar experiments were made with aromatic compounds rich in negative radicles, but not containing nitro-groups, but in no case was any coloured additive compound produced.

When the compound  $C_6H_2(NO_2)_3 \cdot OC_6H_5, C_6H_5ONa$  (Abstr., 1898, i, 517) is heated with methyl alcohol, both the benzyl groups are replaced by methyl, and on treating the methyl compound with benzyl alcohol the reverse change occurs. Benzyl picrate melts at  $145^\circ$ , and not at  $115^\circ$ , as inadvertently stated (*loc. cit.*). Benzoyl chloride reacts with the methyl compound,  $C_6H_2(NO_2)_3 \cdot OMe, OMeNa$ , with the formation of a substance of a more intense scarlet colour.

The paper also contains the description of an improved method for the preparation of picryl chloride. E. G.

**Alkylation of Indene.** By WILHELM MARCKWALD (*Ber.*, 1900, 33, 1504—1505).—The indenenes can be alkylated by the action of alkyl iodides in presence of solid alkali hydroxides.

1 *Benzylindene*,  $CH \leq \overset{C_6H_5}{CH} > CH \cdot CH_2Ph$ , prepared by the action of benzyl chloride and solid potassium hydroxide on indene, is a yellow oil which boils at  $230-235^\circ$  under 15 mm. pressure.

4-*Methylindene* boils at  $197-200^\circ$ , and, unlike indene, is lighter



than water; it gives a series of colour reactions with sulphuric acid, which serve to distinguish it from indene and the isomeric 3-methylindene.  
T. M. L.

**Oxidation of Aniline.** By EUGEN BAMBERGER and FRED. TSCHIRNER (*Annalen*, 1900, **311**, 78—90. Compare Abstr., 1898, i, 518, and Abstr., 1899, i, 347).—The paper describes in detail the experimental results, of which a summary has already appeared (*loc. cit.*).  
M. O. F.

**Direct Introduction of Nitro-groups into the Side Chain of Aromatic Amines.** By EUGEN BAMBERGER and ERNST HOFF (*Annalen*, 1900, **311**, 91—98. Compare Abstr., 1894, i, 239; also Abstr., 1895, i, 261, 273).—The paper contains experimental details relating to the action of nitric anhydride on *o*-toluidine, *p*-toluidine,  $\psi$ -cumidine, and *p*-nitraniline (compare *loc. cit.*).  
M. O. F.

**Dehydration of Amine Nitrates to Nitramines (Diazoic Acids).** By EUGEN BAMBERGER and ERNST HOFF (*Annalen*, 1900, **311**, 99—116).—When the nitrates of certain amines are heated with acetic anhydride, the elements of water are eliminated, and nitramines (diazoic acids) produced (Bamberger, Abstr., 1895, i, 273). The yield of a diazoic acid, depending on its tendency to undergo isomeric change, reaches a maximum in the case of *o*-nitraniline and *p*-nitraniline;  $\alpha$ -naphthylamine and  $\beta$ -naphthylamine do not undergo the change in question.

The course of the reaction has been studied in the case of aniline, *o*-toluidine, *p*-toluidine, *p*-bromoaniline, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, *m*-nitro-*o*-toluidine, *m*-nitro-*p*-toluidine, *p*-chloroaniline, and *p*-chloro-*o*-nitroaniline.  
M. O. F.

**Action of Cyanogen Bromide on Dimethyl- and Diethylaniline.** By ROLAND SCHOLL and WILHELM NÖRR (*Ber.*, 1900, **33**, 1550—1554).—Cyanogen bromide reacts with dimethylaniline at the ordinary temperature to form methyl bromide, which combines with the excess of the dimethylaniline, and *methylecyanoaniline*,  $\text{NMePh}\cdot\text{CN}$ , which crystallises in colourless plates melting at 31—32°; this is also formed by the action of cyanogen bromide on methylaniline. Ethylaniline behaves in a similar manner towards cyanogen bromide, ethylecyanoaniline being produced, together with ethyl bromide, only a small portion of which, however, unites with the excess of the base.  
A. H.

**Molecular Rearrangement of Imino-ethers by Heat.** By WILHELM WISLIZENUS and MAX GOLDSCHMIDT (*Ber.*, 1900, **33**, 1467—1471. Compare Wheeler, this vol., i, 293).—Phenylformiminioethyl ether,  $\text{OEt}\cdot\text{CH}\cdot\text{NPh}$ , when heated in a sealed tube for 8 hours at 230—240°, yields 40 per cent. of the isomeric methylformanilide, a small quantity of diphenylformamidine being also formed; the transformation of phenylformiminioethyl ether into ethylformanilide is somewhat more complete (65 per cent.) under similar conditions, whilst phenylbenziminomethyl ether,  $\text{OMe}\cdot\text{CPh}\cdot\text{NPh}$ , yields 35 per cent. of the theoretical quantity of methylbenzanilide. From these

transformations, it appears that in the alkyl derivatives of the acid amides the stable position of the alkyl radicle is in attachment to nitrogen; the silver derivatives, on the other hand, must be regarded as O-derivatives, since in the cold they give O-ethers, although the application of heat suffices to convert the latter into N-ethers. Since benziminomethyl ether is decomposed, by heating at  $270-280^{\circ}$ , into benzonitrile and methyl alcohol, it appears that the foregoing transformations by heat are fundamentally different to the conversion of imino-ethers into acid amides by warming with alkyl iodides; in the latter case, the change takes place owing to the formation of an intermediate additive compound (Wheeler, *loc. cit.*). W. A. D.

**Action of Cyanogen Bromide on Phenol.** By ROLAND SCHOLL and WILHELM NÖRR (*Ber.*, 1900, 33, 1555).—When phenol is heated at  $130^{\circ}$  with cyanogen bromide, it yields *p*-bromophenol. Resorcinol behaves in a similar manner, yielding monobromoresorcinol.

A. H.

**Nitroso-orcinol.** By FERDINAND HENRICH (*Ber.*, 1900, 33, 1433—1435. Compare Abstr., 1896, i, 476; 1897, i, 404; and this vol., i, 163).—The red ( $\beta$ ) variety, as prepared by the author's method, is probably as pure as that prepared by Farmer and Hantzsch (this vol., i, 103), for it changes comparatively suddenly into the yellow ( $\alpha$ ) variety at  $126-129^{\circ}$  if only a whole crystal of it be heated. When the powdered substance is heated, the change occurs at  $90-110^{\circ}$ , a partial change having taken place during the powdering. The author's value of the dissociation constant of the yellow variety differs more from that of Farmer and Hantzsch than might be expected, and it is not impossible that the latter were working with the red variety.

C. F. B.

**Reactions of Formaldehyde.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1900, 24, 145. Compare this vol., i, 285).—*Anhydro-p-acetylaminobenzyl alcohol* is formed when acetanilide is boiled with excess of formaldehyde (40 per cent.) and a little dilute sulphuric acid for some time, and the red liquid thus obtained treated with alkali; it is best purified by solution in chloroform and precipitation with ether.

When resorcinol is treated with an excess of formaldehyde in the presence of dilute mineral acids, a reddish-brown compound,  $C_{17}H_{16}O_6$ , is obtained; it is insoluble in all the ordinary solvents; acids turn it brick-red, and alkalis purple-red (compare Caro, Abstr., 1892, 855).

J. J. S.

**Action of Formaldehyde on Methylaniline.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1900, 24, 284. Compare this vol., i, 285, and preceding abstract).—When monomethylaniline is treated with an excess of formaldehyde in the presence of hydrochloric acid, colourless crystals are obtained; these dissolve in water, and are reprecipitated on the addition of hydrochloric acid. Alkalis convert the crystals into amorphous *p-anhydromethylaminobenzyl alcohol*,  $CH_2:C_6H_4:NMe$ ,

which dissolves in chloroform, but is insoluble in ether, and melts and decomposes at  $196^{\circ}$ . J. J. S.

**Benzoyl Hydrogen Peroxide.** Oxidation of Benzaldehyde in Air. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 1569—1585).—Benzoyl peroxide was prepared by the action of benzoyl chloride and sodium hydroxide on hydrogen peroxide (von Pechmann and Vanino, *Abstr.*, 1894, i, 416), and when purified by dissolving in chloroform and precipitating with methyl alcohol was found to be without odour, and only very slightly soluble in water. On adding alcoholic sodium ethoxide to an ethereal solution of the peroxide, it was converted into ethyl benzoate and *benzoyl sodium peroxide*,  $C_6H_5 \cdot CO \cdot O \cdot ONa$ , which separated as a fine powder. This was dissolved in water, acidified, and extracted with chloroform, when a crude *benzoyl hydrogen peroxide*,  $C_6H_5 \cdot CO \cdot O \cdot OH$ , was obtained; when pure, this forms crystals melting without decomposition at  $41-43^{\circ}$ , liquefies in contact with water to a heavy oil, but is moderately stable when dry, and does not liquefy in air, dissolves easily in all solvents except light petroleum, from which it separates in leaflets, sublimes readily at the ordinary temperature, distils at  $97-110^{\circ}$  under 13—15 mm. pressure, leaving behind a certain amount of benzoic acid as a product of decomposition, and decomposes completely into benzoic acid when heated to  $80-100^{\circ}$  in the air. Unlike benzoyl peroxide, it has a strong, unpleasant odour resembling that of hypochlorous acid rather than that of ozone, and the vapour turns starch-iodide paper blue. It does not explode when struck, and decomposes without violence when heated; it is not decomposed by manganese dioxide, silver, or platinum, and does not oxidise chromic acid; it liberates iodine from an acid solution of potassium iodide, and more slowly from a solution to which a bicarbonate has been added, oxidises sulphurous acid, hydrochloric acid, ferrous acetate, and manganous acetate, turns litmus red and gradually bleaches it, decolorises indigo-tincture very rapidly, oxidises aniline to nitrosobenzene, benzaldehyde to benzoic acid, and menthone to mentholactone, but does not act on acetone or camphor. With benzoyl chloride and sodium hydrogen carbonate, it gives benzoyl peroxide, whilst with acetic anhydride it gives acetyl benzoyl peroxide. An *acid sodium salt* is produced by the action of carbonic, acetic, or sulphuric acid on the neutral sodium salt; it separates as a thick paste of flaky crystals, and soon decomposes into oxygen, sodium benzoate, and benzoic peroxide.

It is suggested that in the spontaneous oxidation of benzaldehyde in air, the first product is benzoyl hydrogen peroxide, and that this usually oxidises another molecule of benzaldehyde to benzoic acid, so that  $10C_6H_5 \cdot CHO$  is oxidised by 1 atom of oxygen; if indigo is present, however, the benzoyl hydrogen peroxide oxidises this in preference to benzaldehyde, and  $10C_6H_5 \cdot CHO$  requires  $O_2$  for oxidation; similarly, in presence of acetic anhydride, acetyl benzoyl peroxide is produced (Nef, *Abstr.*, 1898, i, 109), and  $10C_6H_5 \cdot CHO$  again requires  $O_2$  for oxidation; the occurrence of these changes has been verified by experiment.

T. M. L.

Action of Aldehydes on Phenylacetic Acid and Benzyl Cyanide and some of its Derivatives with the Formation of Stilbene and Stilbene Derivatives. By REINHOLD VON WALTHER and A. WETZLICH (*J. pr. Chem.*, 1900, [ii], **61**, 169—198. Compare Abstr., 1898, i, 321).—Details are now given for the preparation of stilbene from benzaldehyde and phenylacetic acid. When treated with silver nitrate in acetic acid solution, stilbene dibromide yields *hydrobenzoin dinitrate*, which is a colourless, microcrystalline powder melting at 132°. Anisaldehyde and phenylacetic acid, when heated together for 8 hours in a sealed tube at 240°, give a 20 per cent. yield of *p*-methoxystilbene. In a similar manner, cuminaldehyde and salicylaldehyde condense with phenylacetic acid to form *p*-isopropylstilbene and 4-phenylcoumarin respectively.

*p*-Nitrophenylacetic acid condenses (a) with benzaldehyde to form *α*-*p*-nitrophenylcinnamic acid, which crystallises in needles melting at 224·5°, forms insoluble silver, copper, lead, ferrous and ferric salts, an ethyl ester melting at 86°, and a methyl ester melting at 104°, but does not yield nitrostilbene when heated; (b) with anisaldehyde to form *p*-methoxy-*p*-nitrostilbene, which crystallises in lustrous, golden leaflets melting at 133°; (c) with cuminaldehyde to form *p*-isopropyl-*p*-nitrostilbene, which crystallises in small, lustrous, deep yellow leaflets melting at 132°; and (d) with salicylaldehyde to form *p*-nitro-4-phenylcoumarin, which forms yellow crystals melting at 262°.

*p*-Chlorobenzyl cyanide condenses (a) with benzaldehyde to form *α*-*p*-chlorophenylcinnamionitrile, which forms colourless prisms melting at 112·5°; (b) with anisaldehyde to form *α*-*p*-chlorophenyl-*p*-methoxycinnamionitrile, which crystallises in broad prisms melting at 127·5°, and yields a dibromide which forms colourless, silky prisms which melt at 164·5°; (c) with furfuraldehyde to form *β*-furfuryl-*α*-*p*-chlorophenylacrylonitrile, which crystallises in long, yellowish, matted needles melting at 80°; (d) with piperonaldehyde to form *α*-*p*-chlorophenylmethylenedioxcinnamionitrile, which melts at 165°; (e) with *o*-nitrobenzaldehyde to form *α*-*p*-chlorophenyl-*o*-nitrocinnamionitrile, which forms bright green aggregates of silky, hair-like crystals melting at 161°; (f) with *m*-nitrobenzaldehyde to form *α*-*p*-chlorophenyl-*m*-nitrocinnamionitrile, which crystallises in yellow, prismatic plates melting at 191°; (g) with *p*-nitrobenzaldehyde to form *α*-*p*-chlorophenyl-*p*-nitrocinnamionitrile, which forms yellow needles melting at 166°; (h) with cuminaldehyde to form *α*-*p*-chlorophenyl-*p*-isopropylcinnamionitrile, which crystallises in plates or tablets frequently twinned, which melt at 126°; and (i) with bromoanisaldehyde to form *α*-*p*-chlorophenyl-*p*-methoxybromocinnamionitrile, which melts at 164°. The condensation products of piperonaldehyde with benzyl cyanide and *p*-nitrobenzyl cyanide melt at 122° and at 187° respectively.

iso-Nitroso-*p*-chlorobenzyl cyanide,  $C_6H_4Cl \cdot C(CN) : NOH$ , obtained by the action of amyl nitrite on *p*-chlorobenzyl cyanide, crystallises in concentric groups of needles, melts at 110°, and forms an unstable silver, but more stable sodium and copper derivatives.

Ethyl *p*-chlorophenylacetate crystallises in needles, melts at 32°.

and boils at  $260^{\circ}$ . The corresponding *methyl* ester is liquid and boils above  $200^{\circ}$ . *p*-Chlorophenylacetic acid condenses with aromatic aldehydes to form stilbene derivatives, but the intermediate acid compounds cannot be obtained; it condenses (a) with benzaldehyde to form *p-chlorostilbene*, which crystallises from glacial acetic acid and melts at  $129^{\circ}$ ; (b) with anisaldehyde to form *p-methoxy-p-chlorostilbene*, which crystallises in leaflets melting at  $177.5^{\circ}$ , and forms a *dibromide* which crystallises in small, white needles; (c) with salicylaldehyde to form *3-p-chlorophenylcoumarin*, which crystallises in clusters of reddish prisms melting at  $184^{\circ}$ ; and (d) with bromoanisaldehyde (which melts at  $52^{\circ}$ ) to form *p-methoxybromostilbene*, which crystallises in lustrous leaflets melting at  $138^{\circ}$ . R. H. P.

**New Drugs.** [Aromatic Hydroxy-acids and Esters.] By ALFRED EINHORN (*Annalen*, 1900, 311, 26—77).—This paper is the first of a series having a similar character, and describes experiments undertaken with the object of introducing new drugs, and of examining certain of those already known with the view of nullifying disagreeable after-effects.

[With BALTHASAR PFYL.]—*Methyl o-hydroxy-m-aminobenzoate* crystallises from a mixture of benzene and petroleum in white needles, and melts at  $90^{\circ}$ ; the *ethyl* ester crystallises from alcohol, and melts at  $47^{\circ}$ .

*p-Amino-m-hydroxybenzoic acid*, prepared by reducing Griess' *p*-nitro-*m*-hydroxybenzoic acid with tin and hydrochloric acid, crystallises from dilute alcohol in brown leaflets, and melts at  $216^{\circ}$ ; the *methyl* ester, known commercially as '*orthoform*,' crystallises from benzene or water in silvery leaflets, and melts at  $120$ — $121^{\circ}$ ; this is also obtained by reducing *methyl p-nitro-m-hydroxybenzoate*, which crystallises from alcohol in needles, and melts at  $92^{\circ}$ . The *ethyl* ester crystallises in silvery leaflets, and melts at  $98^{\circ}$ .

*Methyl m-amino-p-hydroxybenzoate*, known commercially as '*orthoform neu*,' is dimorphous, the technical product being in the form of lustrous needles which melt at  $142^{\circ}$ ; it also separates from chloroform in white crystals which melt at  $110$ — $111^{\circ}$ , and after solidification at  $142^{\circ}$ . The *hydrochloride* of this salt crystallises from alcohol in white needles and melts at  $225^{\circ}$ . The *ethyl* ester is likewise dimorphous, crystallising from chloroform with a small proportion of petroleum in aggregates of lustrous needles melting at  $84^{\circ}$ , whilst glacial acetic acid deposits it in leaflets melting at  $112^{\circ}$  (compare Auwers and Röhrig, *Abstr.*, 1897, i, 341).

*Ethyl nitro-o-cresotate* [ $\text{NO}_2:\text{Me}:\text{OH}:\text{CO}_2\text{H} = 5$  or  $6:3:2:1$ ], prepared by the action of nitric acid in glacial acetic acid on *ethyl cresotate* in the same solvent, crystallises from dilute alcohol in slender plates and melts at  $63$ — $61^{\circ}$ . *Ethyl amino-o-cresotate*, obtained on reducing the foregoing ester with tin and hydrochloric acid, crystallises from dilute alcohol in slender needles and melts at  $102^{\circ}$ .

*Ethyl nitro-m-cresotate* crystallises from dilute alcohol in slender, white needles, and melts at  $73$ — $74^{\circ}$ ; *ethyl amino-m-cresotate*, obtained from it on reduction, crystallises from alcohol in long, white needles melting at  $85^{\circ}$ , and therefore differs from the *ethyl aminocresotate* described by Gattermann (*Abstr.*, 1894, i, 504), which melts at  $71$ — $72^{\circ}$ .

*Nitro-p-cresotic acid* crystallises from benzene or dilute alcohol in slender, reddish-yellow needles, and melts at  $175^{\circ}$ ; the *ethyl* ester forms lustrous, pale yellow leaflets, and melts at  $104\text{--}105^{\circ}$ . *Ethyl amino-p-cresotate* separates from alcohol in white needles and melts at  $101^{\circ}$ .

3-Hydroxy-*o*-toluic acid [ $\text{CO}_2\text{H}:\text{Me}:\text{OH}=1:2:3$ ] melts at  $145\text{--}146^{\circ}$ ; when dissolved in glacial acetic acid and treated with a mixture of glacial acetic and concentrated nitric acids, it yields two nitro-derivatives.

*a*-Nitro-3-hydroxy-*o*-toluic acid crystallises from dilute alcohol in slender, yellow needles, and melts at  $182^{\circ}$ . Reduction with tin and hydrochloric acid converts it into *a*-amino-3-hydroxy-*o*-toluic acid, which crystallises from water in aggregates of needles, and melts at  $202\text{--}204^{\circ}$ , when it decomposes; the *methyl* and *ethyl* esters melt at  $129^{\circ}$  and  $109\text{--}110^{\circ}$  respectively.

$\beta$ -Nitro-3-hydroxy-*o*-toluic acid crystallises from water in aggregates of prisms, and softens at  $100^{\circ}$ , afterwards becoming solid, and finally melting at  $208^{\circ}$ , when it darkens and evolves gas. Reduction converts it into  $\beta$ -amino-3-hydroxy-*o*-toluic acid, which crystallises from water in prisms, and melts at  $221\text{--}222^{\circ}$ ; its probable constitution [ $\text{CO}_2\text{H}:\text{Me}:\text{OH}:\text{NH}_2=1:2:3:6$ ] is indicated by the fact that it does not yield esters when the alcoholic solutions are treated with mineral acids.

*Ethyl* 3-hydroxy-*o*-toluate forms prismatic crystals, and melts at  $69^{\circ}$ . Nitration yields two derivatives, of which *ethyl*  $\beta$ -nitro-3-hydroxy-*o*-toluate is less readily soluble in water, and melts at  $143\text{--}145^{\circ}$ ; reduction converts this substance into *ethyl*  $\beta$ -amino-3-hydroxy-*o*-toluate, which crystallises from benzene in aggregates of pale yellow, feathery crystals and melts at  $113^{\circ}$ . *Ethyl a-nitrohydroxytoluate* forms yellow needles and melts at  $72^{\circ}$ .

5-Hydroxy-*o*-toluic acid [ $\text{CO}_2\text{H}:\text{Me}:\text{OH}=1:2:5$ ] melts at  $183\text{--}184^{\circ}$ , Kalle and Jacobsen giving  $179^{\circ}$  and  $172^{\circ}$  respectively. Nitration converts it into a *nitro-5-hydroxy-*o*-toluic acid*, which crystallises from alcohol in yellow, lustrous needles melting at  $163\text{--}164^{\circ}$ , and  $\beta$ -nitro 5-hydroxy-*o*-toluic acid, separating from ethyl acetate in yellow prisms which melt at  $196\text{--}197^{\circ}$ ; the *ethyl* esters are obtained from ethyl 5-hydroxy-*o*-toluate by direct nitration, the  $\beta$ -compound being an oil, whilst the  $\alpha$  ester crystallises from alcohol in yellow needles and melts at  $77\text{--}79^{\circ}$ . Tin and alcoholic hydrochloric acid reduce the esters to the corresponding amino-compounds, of which the  $\alpha$ -derivative melts at  $92\text{--}94^{\circ}$ ; the  $\beta$ -compound melts at  $52^{\circ}$  and forms a crystalline hydrochloride which melts and decomposes at  $110\text{--}111^{\circ}$ .

*Ethyl nitroprotocatechuate* crystallises from chloroform in aggregates of needles and melts at  $165^{\circ}$ . Reduction converts it into *ethyl aminoprotocatechuate*, which separates from a mixture of benzene and petroleum in pale pink needles and melts at  $89\text{--}90^{\circ}$ ; the *hydrochloride* forms white leaflets melting at  $220^{\circ}$ .

*Methyl nitroguaiacolcarboxylate*, prepared by adding a mixture of glacial acetic and concentrated nitric acids to a solution of methyl guaiacolcarboxylate in glacial acetic acid, crystallises from dilute alcohol in yellow needles melting at  $135^{\circ}$ . *Methyl aminoguaiacolcarb-*

*oxylate* separates from benzene in long, yellow needles and melts at  $130^{\circ}$ .

*Ethyl nitrodimethyl- $\alpha$ -resorcylate* [ $\text{COEt}:\text{NO}_2:(\text{OMe})_2 = 1:4:3:5$ ] forms pale yellow needles melting at  $130^{\circ}$ . *Ethyl aminodimethyl- $\alpha$ -resorcylate*, prepared by reducing the foregoing ester, crystallises from ether in aggregates of needles melting at  $49\text{--}50^{\circ}$ ; the hydrochloride separates from acetone in white needles.

*Methyl nitro- $\alpha$ -naphtholcarboxylate* crystallises from glacial acetic acid in small, yellowish needles and melts at  $161^{\circ}$ ; reduction converts it into *methyl amino- $\alpha$ -naphtholcarboxylate*, melting at  $128\text{--}129^{\circ}$ .

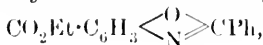
*Methyl 8-hydroxyquinolinecarboxylate* crystallises from benzene in white prisms and melts at  $140^{\circ}$ ; the *ethyl* ester melts at  $87^{\circ}$ . When a mixture of nitric and glacial acetic acids is added to a solution of the methyl salt in acetic acid, the *acetate* of methyl nitro-8-hydroxyquinolinecarboxylate crystallises in yellow needles; at  $100^{\circ}$ , this compound loses acetic acid, yielding *methyl nitro-8-hydroxyquinolinecarboxylate*, which crystallises from alcohol in aggregates of small needles and melts at  $191^{\circ}$ . Reduction gives rise to *methyl amino-8-hydroxyquinolinecarboxylate*, which is deposited by benzene in groups of minute needles melting at  $120\text{--}121^{\circ}$ .

*Methyl 5-nitro-2-benzoyloxybenzoate*, prepared by the action of benzoyl chloride on methyl 5-nitrosalicylate, crystallises from alcohol or petroleum in large, well-formed prisms melting at  $117\text{--}118^{\circ}$ ; unlike the substance from which it is prepared, and which also melts at  $117^{\circ}$ , the benzoyl derivative is insoluble in sodium hydroxide. *Methyl 5-amino-2-benzoyloxybenzoate* separates from alcohol in six-sided plates or prisms and melts at  $176^{\circ}$ .

*Ethyl 3-nitro-4-acetoxybenzoate* crystallises from dilute alcohol or acetic acid in silvery leaflets and melts at  $39^{\circ}$ . Reduction converts it into *ethyl 1-methylbenzoxazole-4-carboxylate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_3\langle\text{O}\rangle_{\text{N}}\text{CMe}$ , which separates from ether in slender, white needles and melts at  $50^{\circ}$ ; treatment with boiling acetic acid or dilute alcohol adds the elements of water to this compound, producing *ethyl 3-acetylamino-4-hydroxybenzoate*, crystallising in aggregates of minute rhombs or prisms and melting at  $199^{\circ}$ . The latter substance may be reconverted into the anhydro-ester by heating it with zinc chloride in an oil-bath.

*Ethyl 3-nitro-4-isobutyroxybenzoate* is a colourless oil yielding, on reduction, *ethyl 3-isobutyrylamino-4-hydroxybenzoate*, which crystallises from alcohol or benzene in white needles melting at  $135\text{--}136^{\circ}$ ; the neutral product of reduction is *ethyl 1-isopropylbenzoxazole-4-carboxylate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_3\langle\text{O}\rangle_{\text{N}}\text{C}\cdot\text{Pr}\beta$ , which boils at  $20^{\circ}$  in a vacuum.

*Methyl 3-nitro-4-benzoyloxybenzoate* crystallises from alcohol in white needles and melts at  $95^{\circ}$ . Reduction converts it into *methyl 3-benzoylamino-4-hydroxybenzoate*, which separates from methyl alcohol in aggregates of leaflets and melts at  $241^{\circ}$ ; the neutral product of reduction is *methyl 1-phenylbenzoxazole-4-carboxylate*,



which crystallises from alcohol in white needles and melts at 157—158°.

[With Hugo Hütz.]—4-*i*-Amylamino-3-hydroxybenzoic acid, prepared by gradually adding 'orthoform' dissolved in amyl alcohol to a small proportion of boiling alcohol, into which sodium is being thrown in small quantities, crystallises from benzene in white needles melting at 171—172°, and forms the *nitroso*-derivative melting at 152—153°; the *ethyl* ester crystallises in white needles and melts at 108—109°.

3-*i*-Amylamino-4-hydroxybenzoic acid, prepared in the same way from methyl *m*-amino-*p*-hydroxybenzoate, the structural isomeride of 'orthoform,' is a brown, amorphous compound yielding a crystalline *hydrochloride* which decomposes at 238°. The *nitroso*-derivative forms lustrous, pink leaflets and decomposes at 157—158°; the *ethyl* ester crystallises from benzene, on adding petroleum, in brownish needles melting at 69—71°. M. O. F.

Formation of Chains. L. The Three Sodium Nitrophenoxides. By CARL A. BISCHOFF [and, in part, FRÄNKEL, GOHS, and WENGEL] (*Ber.*, 1900, 33, 1591—1602).—*Ethyl α-o-nitrophenoxypropionate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol in needles and melts at 48°; the *acid* crystallises from dilute alcohol in pale yellow needles and melts at 157—159°; *methylphenomorpholone*,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{O} \text{---} \text{CHMe} \end{smallmatrix}$ , prepared by reducing the ester with zinc dust and hydrochloric acid, crystallises from dilute alcohol in minute needles, melts at 143—144°, and dissolves readily in most organic solvents, or in strong acids. The *m-ester* is a heavy, brownish oil, which boils with partial decomposition at 187° under 7 mm., and at 295—296° under 769 mm. pressure; the *m-acid* forms yellow needles, melts at 107—110°, and decomposes gradually in the air. The *p-ester* crystallises from alcohol in small, colourless needles, melts at 59—61·5°, and boils at 195·5° under 4 mm. pressure; the *p-acid* crystallises from ether and benzene in colourless, felted needles and melts at 142·5—143°.

*Ethyl α-o-nitrophenoxybutyrate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$ , melts at 40° and resembles the propionate; the *acid* crystallises from dilute alcohol in pale yellowish flakes and melts at 99—101°; on reducing with zinc dust and hydrochloric acid, chlorination takes place, and *ethyl chlorophenomorpholone*,  $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{O} \text{---} \text{CHEt} \end{smallmatrix}$ , is produced; this crystallises from alcohol in colourless needles and melts at 144—146°. The *m-ester* is a yellow oil which boils with partial decomposition at 184·5° under 5 mm. pressure; the *m-acid* crystallises from a mixture of ether and light petroleum in aggregates of yellow needles, melts at 94·5—95·5°, and decomposes on exposure to the air. The *p-ester* is a clear, yellow oil, and boils at 207—208° under 18 mm. pressure; the *acid* crystallises from hot water in flakes or needles and melts at 116°.

*o-Nitrophenyl isobutyrate*,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , prepared by the action of isobutyryl chloride on sodium *o*-nitrophenoxide, is a yellow oil and boils at 163—164° under 9 mm. pressure.

*Ethyl α-m-nitrophenoxyisobutyrate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$ , is a



yellow oil and boils at  $175.8^{\circ}$  under 5 mm. pressure; the *acid* crystallises from a mixture of ether and light petroleum in yellow prisms and melts at  $97.7-98^{\circ}$ . The *p-ester* is an oil which boils at  $190^{\circ}$  under 13 mm. pressure; the *acid* crystallises from hot water in prisms.

*Ethyl  $\alpha$ -o-nitrophenoxysisovalerate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHPr}^s \cdot \text{CO}_2\text{Et}$ , is an oil which boils at  $198-208^{\circ}$  under 8 mm. pressure; the *acid* crystallises in needles and melts at  $83-85^{\circ}$ . The *m-ester* is a yellowish-brown oil, and boils at  $187^{\circ}$  under 6.5 mm. pressure; the *acid* crystallises from light petroleum in long, colourless needles and melts at  $82^{\circ}$ . The *p-ester* is a yellow oil boiling at  $195-205^{\circ}$ ; the *acid* crystallises from alcohol in pale yellow flakes and melts at  $134-135^{\circ}$ .

T. M. L.

**Formation of Chains. LI. Chloro- and Bromo-phenols.** Summary of Quantitative Results on the Condensation of Phenols with Esters of  $\alpha$ -Bromo-fatty Acids. By CARL A. BISCHOFF [and, in part, HERR, JENTSCHMEN, and SSVROTSCHIKIN] (*Ber.*, 1900, 33, 1603-1611).—*Ethyl  $\alpha$ -2:4-dichlorophenoxypropionate*,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , is a yellowish oil and boils at  $173-176^{\circ}$  under 12 mm. pressure; the *acid* crystallises from acetone in large prisms, and melts at  $117-118^{\circ}$ .

*Ethyl  $\alpha$ -2:4-dichlorophenoxyisobutyrate*,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$ , is a colourless liquid with a faint odour; the *acid* did not solidify in 5 years.

*Ethyl 2:4:6-trichlorophenoxyacetate*,  $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol in needles and melts at  $41^{\circ}$ ; the *acid* crystallises from dilute alcohol in minute, felted, colourless needles and melts at  $177^{\circ}$ .

*Ethyl 2:4:6-tribromophenoxyacetate* crystallises from light petroleum in colourless needles and melts at  $81^{\circ}$ . The *acid* crystallises from dilute alcohol in needles and melts at  $200^{\circ}$ .

The paper contains a summary of all the quantitative measurements on the condensation of phenols with esters of the  $\alpha$ -bromo-fatty acids, and the influence of the various substituting groups is discussed in detail.

T. M. L.

**Catecholacetic Acid.** By H. LUDEWIG (*J. pr. Chem.*, 1900, [ii], 61, 345-380).—The salts and a number of derivatives of catecholacetic acid (D. R. P. 87,336) are described. The *methyl ester*,  $\text{OH} \cdot \text{C}_6\text{H}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , crystallises from light petroleum in long felted needles which melt at  $59^{\circ}$ , and contain rather more than  $\text{H}_2\text{O}$ ; the anhydrous ester is a colourless, hygroscopic oil which readily passes into the hydrated crystalline form. The *ethyl ester* crystallises from light petroleum in white tablets, melts at  $53^{\circ}$ , and on further heating loses alcohol and is converted into the lactone which begins to distil at  $237^{\circ}$ .

*Acetylcatecholacetic acid*,  $\text{OAc} \cdot \text{C}_6\text{H}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises from benzene in small, white needles, melts at  $110^{\circ}$  and on heating is converted into acetic acid and the lactone.

Phosphorus trichloride converts the acid into the lactone and not into the acid chloride.

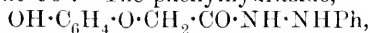
*Catecholacetamide*,  $\text{OH} \cdot \text{C}_6\text{H}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , prepared by heating

the ammonium salt formed by the action of alcoholic ammonia on the methyl ester or by the action of dry ammonia on an ethereal solution of the lactone, crystallises from alcohol in stout, colourless prisms, melts at  $108^{\circ}$  and contains  $1\text{H}_2\text{O}$ , but is converted by fusion into the anhydrous amide which crystallises from benzene and melts at  $130^{\circ}$ .

*Catecholacetanilide* crystallises from alcohol in long, silky needles, melts at  $161^{\circ}$ , and distils at  $250^{\circ}$ ; it gives no coloration with ferric

chloride and probably has the constitution  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \cdot \text{CO} \\ \diagdown \quad | \\ \text{O} \text{---} \text{NH}_2 \cdot \text{Ph} \end{smallmatrix}$ ;

the *acetyl* derivative,  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from benzene in minute, white needles and melts at  $105^{\circ}$ ; the *benzoyl* derivative crystallises from alcohol in long, white needles and melts at  $117^{\circ}$ . The *p-toluidide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , crystallises from alcohol in white flakes and melts at  $147^{\circ}$ . The *o-toluidide* crystallises from benzene in white needles, melts at  $105^{\circ}$ , and distils at  $220^{\circ}$ . The *methylanilide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NMePh}$ , separates from ether in large, colourless, rhombic crystals and melts at  $95^{\circ}$ . The *piperidide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_5\text{NH}_{10}$ , crystallises from alcohol in large, colourless tablets and melts at  $98^{\circ}$ . The phenylhydrazide,



crystallises from alcohol in white, glistening flakes, melts at  $191^{\circ}$ , and is probably identical with the substance prepared by Moureu (Abstr., 1899, i, 125) by the action of phenylhydrazine acetate on catecholacetic acid.

*Ethyl dinitrocatecholacetate*,  $\text{OH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , produced by the action of nitrous acid on an alcoholic solution of catecholacetic acid, crystallises from dilute alcohol in white, glistening flakes which melt at  $88^{\circ}$  and contain  $1\text{H}_2\text{O}$ , whilst the anhydrous ester is yellow and melts at  $79^{\circ}$ . In acetic acid solution, nitrous acid converts catecholacetic acid into dinitrocatecholacetic acid and then into oxalic acid. *Dinitrocatecholacetanilide*,  $\text{OH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , prepared by the action of nitrous acid on an alcoholic solution of catecholacetanilide, crystallises from alcohol in yellow, felted needles, and melts at  $199^{\circ}$ .

*Nitrocatecholacetic acid*, prepared by the action of nitric acid (1 mol.) on a solution of catecholacetic acid in acetic acid, crystallises from water in white, felted needles and melts at  $183^{\circ}$ . *Dinitrocatecholacetic acid*, prepared in a similar manner, crystallises from water in small, yellow needles which melt at  $122^{\circ}$  and contain  $1\text{H}_2\text{O}$ ; the anhydrous acid separates from benzene in yellow crystals and melts at  $147^{\circ}$ .

*Bromocatecholacetic acid*, prepared by the action of bromine (1 mol.) on an ethereal solution of catecholacetic acid, crystallises from water in white needles and melts at  $158^{\circ}$ ; the *ethyl* ester crystallises from dilute alcohol in long, colourless prisms and melts at  $48^{\circ}$ . *Ethyl dibromocatecholacetate* crystallises from dilute alcohol in white tablets which melt at  $89^{\circ}$  and contain  $\frac{1}{2}\text{H}_2\text{O}$ ; the anhydrous ester melts at  $69^{\circ}$ ; the *acid* crystallises from water in minute, white needles and melts at  $158^{\circ}$ ; the *lactone*,  $\text{C}_6\text{H}_2\text{Br}_2 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \diagdown \quad | \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$ , crystallises from light petroleum and melts at  $106^{\circ}$ . *Ethyl tribromocatecholacetate* crystallises

in white flakes and melts at  $118^{\circ}$ . *Ethyl tetrabromocatecholacetate*,  $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , crystallises from alcohol in minute, white needles and melts at  $153^{\circ}$ ; the *acid* separates from ether as a white powder and melts with decomposition at  $231^{\circ}$ . T. M. L.

**Dichlorophthalic Acids: Products of Condensation.** By ÉMILE C. SEVERIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 374—382).—3:4-Dichloro-2'-dimethylaminobenzoylbenzoic acid and its derivatives have been already described (this vol., i, 296); when reduced with zinc and hydrochloric acid, this acid yields the corresponding 3:4'-dichloro-2'-dimethylaminobenzylbenzoic acid,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$ , which crystallises in slender, white needles melting at  $225^{\circ}$ . N. L.

**Formation of Chains. LII. Derivatives of Catechol.** By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1669—1676).—The quantitative results obtained by treating the disodium derivatives of catechol with the calculated quantity of ethyl  $\alpha$ -bromopropionate, ethyl  $\alpha$ -bromobutyrate, ethyl  $\alpha$ -bromoisobutyrate, and ethyl  $\alpha$ -bromoisovalerianate are tabulated. *Diethyl catecho-bis- $\alpha$ -oxypropionate*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et})_2$ , is a yellow oil with a garlic-like odour and boils at  $201^{\circ}$  under 6 mm. pressure. *Catecho- $\alpha$ -oxypropionolactone*, obtained as a bye-product in the preparation of the ethyl ester, crystallises in colourless plates melting at  $51\text{--}51\cdot5^{\circ}$ ; when hydrolysed, these compounds yield two stereo-isomeric *catecho-bis- $\alpha$ -oxypropionic acids*, one of which crystallises in well-formed plates melting at  $167\text{--}168^{\circ}$ , and the other in aggregates of slender needles melting at  $145\cdot5\text{--}146^{\circ}$ ; both acids, when distilled, yield the lactone and small quantities of lactic acid, and when treated with *p*-phenetidine yield *catecho-bis- $\alpha$ -oxypropionyl-*p*-diphenetide*, which crystallises in small, soft needles melting at  $186\text{--}187^{\circ}$ . *Catecho-bis- $\alpha$ -oxypropionic acid mono-*p*-phenetide* crystallises in large prisms melting at  $169\text{--}170^{\circ}$ , and *catecho-mono- $\alpha$ -oxypropionyl-*p*-phenetide* crystallises, with  $2\text{H}_2\text{O}$ , in large prisms melting at  $163\cdot5^{\circ}$ .

*Diethyl catecho-bis- $\alpha$ -oxybutyrate* is a bright yellow oil which boils at  $290\text{--}330^{\circ}$  under 744 mm. pressure, and at  $195\text{--}225^{\circ}$  under 13 mm. pressure, and, when hydrolysed, yields an oily *acid*, which, when distilled, forms the *anhydride*, which is an oil boiling at  $240\text{--}250^{\circ}$  under 107 mm. pressure; *catecho-mono- $\alpha$ -oxybutyrolactone*, obtained as a bye-product in the preparation of the ethyl ester, is a bright yellow oil which boils at  $120\text{--}130^{\circ}$  under 6 mm. pressure.

*Diethyl catecho-bis- $\alpha$ -oxyisobutyrate* is a bright yellow oil boiling at  $197^{\circ}$  under 27 mm. pressure; *catecho-mono- $\alpha$ -oxyisobutyrolactone* forms colourless crystals melting at  $49\cdot5\text{--}50\cdot5^{\circ}$ ; the ethyl ester, when hydrolysed, yields the oily *acid*, which boils at  $221^{\circ}$  under 24 mm. pressure, but is then partly converted into the *anhydride*, which crystallises in six-sided plates melting at  $188\text{--}188\cdot5^{\circ}$ .

*Diethyl catecho-bis- $\alpha$ -oxyisovalerate* is a yellow oil which boils at  $210\text{--}215^{\circ}$  under 48 mm. pressure, and when hydrolysed yields the *anhydride*, which boils at  $230\text{--}240^{\circ}$  under 20 mm.; *catecho-mono- $\alpha$ -oxyisovalerolactone* is a bright, yellow oil, which boils at  $250\text{--}260^{\circ}$  under 753 mm. pressure.

R. H. P.

**Formation of Chains. LIII. Derivatives of Resorcinol and Orcinol.** By CARL A. BISCHOFF [and, in part, ABRAMSON, AGROZKIN, and MINSKI] (*Ber.*, 1900, 33, 1676—1686).—Quantitative experiments with the disodium derivatives of resorcinol and orcinol analogous to those described in the preceding abstract are tabulated.

*Diethyl resorcino-bis- $\alpha$ -oxypropionate* is a thick, yellow oil which partly solidifies in the cold to needle-shaped crystals melting at  $72.5^\circ$ , boils at  $202\text{--}204^\circ$  under 13 mm. pressure, and when hydrolysed yields the corresponding *acid*, which crystallises, with  $1\frac{1}{2}\text{H}_2\text{O}$ , in colourless, lustrous needles melting at  $226^\circ$ ; it is probable that both these are mixtures of stereoisomeric compounds.

*Diethyl resorcino-bis- $\alpha$ -oxybutyrate* is an oil boiling between  $205^\circ$  and  $240^\circ$  under 55 mm. pressure, and when hydrolysed yields the corresponding *acid*, which crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$ , melts at  $111^\circ$ , boils at  $220\text{--}230^\circ$  under 150 mm. pressure, and forms a *calcium* salt which is a yellow powder containing  $3\text{H}_2\text{O}$ .

*Diethyl resorcino-bis- $\alpha$ -oxyisobutyrate* is a bright yellow, viscous oil which boils at  $208\text{--}209^\circ$  under 4 mm. pressure, and, when hydrolysed, yields an indefinite *acid*, which decomposes on distillation under reduced pressure.

*Diethyl resorcino-bis- $\alpha$ -oxyisovalerate* is a bright yellow oil, which boils at  $200\text{--}206^\circ$  under 20 mm. pressure, and, when hydrolysed, yields the corresponding *acid*, which boils at  $230\text{--}240^\circ$  under 85 mm. pressure.

*Diethyl orcino-bis- $\alpha$ -oxypropionate*,  $\text{C}_6\text{H}_3\text{Me}(\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et})_2$ , is a yellow oil with a garlic-like odour, which boils at  $314\text{--}317.5^\circ$  under 764 mm. pressure, and, when hydrolysed, yields the corresponding *acid*, which sinters at  $137^\circ$  and melts at  $146^\circ$ .

*Diethyl orcino-bis- $\alpha$ -oxybutyrate* is a yellow oil which boils at  $330\text{--}340^\circ$  under 763 mm. pressure, and when hydrolysed yields the corresponding *acid*, which is an oil.

The condensation of disodium orcinoxide and diethyl  $\alpha$ -bromoisobutyrate yields an indefinite *compound*, which boils at  $280\text{--}300^\circ$  under 761 mm. pressure, and, when hydrolysed, yields an oily *acid*. The corresponding *compound* derived from diethyl  $\alpha$ -bromoisovalerate is a yellow oil which boils at  $310\text{--}315^\circ$  under 764 mm. pressure, and when hydrolysed yields an oily *acid*.

R. H. P.

**Formation of Chains. LIV. Derivatives of Quinol.** By CARL A. BISCHOFF [and, in part, OLZEWSKI, BASSEWICZ, STELMANN, and DUNIN-SULGUSTOWSKI] (*Ber.*, 1900, 33, 1686—1692).—Quantitative experiments with disodium quinol, similar to those described in the two preceding abstracts, are tabulated.

*Diethyl quino-bis- $\alpha$ -oxypropionate*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et})_2$ , occurs in two isomeric forms, one of which forms large, colourless crystals melting at  $91\text{--}91.5^\circ$ , and when hydrolysed yields an *acid* melting at  $235^\circ$ , whilst the other is an oil which boils at  $187\text{--}190^\circ$  under 6 mm. pressure, and when hydrolysed yields an isomeric *acid* melting at  $220\text{--}224^\circ$ .

*Diethyl quino-bis- $\alpha$ -oxybutyrate* was obtained as a viscous, bright yellow oil, which could be divided, when distilled, into two fractions

boiling at 210—212° and 212—217° under 10 mm. pressure; the lower fraction, when hydrolysed, yields an *acid* which crystallises in prisms melting at 198—199°, and the higher fraction an *acid* which is an oil.

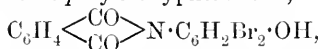
*Diethyl quino-bis- $\alpha$ -oxyisobutyrate* crystallises in long needles melting at 81°, and when hydrolysed yields the corresponding *acid*, which crystallises in long, thin, colourless plates melting at 189°.

*Diethyl quino-bis- $\alpha$ -oxyisovalerate* is a bright yellow oil which boils at 210—215° under 20 mm. pressure, and when hydrolysed yields the corresponding *acid*, which forms plate-shaped crystals melting at 209°.

The paper concludes with a comparison between the various dihydroxybenzenes, which shows that the para-position is best suited to these condensations, and the ortho-position least.

R. H. P.

**Tetrabromophenolphthalein.** By HANS MEYER (*Monatsh.*, 1900, 21, 263—266).—Dibromo-*p*-hydroxyphthalanil,

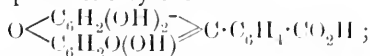


which is formed in small quantity during the production of Friedländer and Stange's tetrabromophenolphthaleinoxime (compare Abstr., 1893, i, 719) becomes the chief product if the proportion of hydroxylamine hydrochloride is increased, or when the oxime is further treated with this reagent. It crystallises in long, slender, colourless needles, is slightly soluble in alcohol, chloroform, or glacial acetic acid, and freely soluble in alkali carbonates or hydroxides. The solution in ammonia becomes blood-red on standing and darkens later. Hydrochloric acid decomposes it, although with difficulty, into phthalic acid and dibromo-aminophenol (compare Abstr., 1899, i, 707). The substance was synthesised by brominating the product of the condensation of phthalic anhydride with *p*-aminophenol. Tetrabromophenolphthalein, which, like the unbrominated phthalein, forms a stable oxime with excess of hydroxylamine hydrochloride, yields phthalimide, if there is no excess (compare Posner's *o*-cyanobenzaldoxime, Abstr., 1897, i, 472).

R. L. J.

**Gallein and Cœrulein.** By WILLIAM R. ORNDORFF and C. E. BREWER (*Amer. Chem. J.*, 1900, 23, 425—431).—Gallein is the phthalein of pyrogallol, as stated by von Baeyer (*Ber.*, 1871, 4, 663), whilst gallin is the corresponding phthalin.

Gallein is best represented by the formula

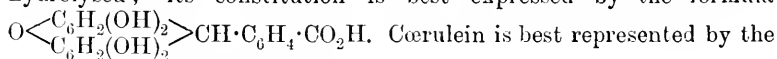


it yields a methyl and an ethyl ester, and a triphenylcarbamate, and also gives coloured tetramethyl and tetraethyl ethers which are easily hydrolysed by solution of sodium carbonate. It also reacts in the tautomeric lactoid form,  $\text{O} \begin{array}{c} \text{C}_6\text{H}_2(\text{OH})_2 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2\text{O}(\text{OH}) \end{array} \text{C} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CO}$ , since it forms a colourless tetracetate, tetrabenzoate, and tetraphenylsulphonate, and also colourless tetramethyl and tetraethyl ethers. The colourless trimethyl ether closely resembles phenolphthalein; it dissolves in sodium carbonate or sodium hydroxide, forming a red solution from which it is precipitated colourless by acids; acetic anhydride converts

it into a colourless acetate which is insoluble in alkalis. The same colourless trimethyl ether results from the hydrolysis of the coloured tetramethyl ether.

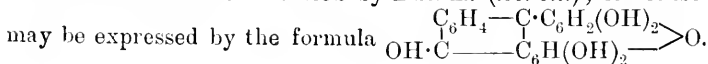
Buchka (Abstr., 1882, 59), has stated that when gallein is reduced it yields hydrogallein, which, on further reduction is converted first into gallin, and finally into gallol. Some doubt was cast on the accuracy of these conclusions by the observations of Herzig (Abstr., 1892, 1319), who was unable to obtain hydrogallein. The present authors find that hydrogallein does not exist, that Buchka's gallol is really gallin, and that his hydrogallein, gallin, and gallol acetates are identical in every respect.

Gallin yields a colourless tetracetate which furnishes a silver salt, and a pentamethyl ether which has no acid properties and is easily hydrolysed; its constitution is best expressed by the formula



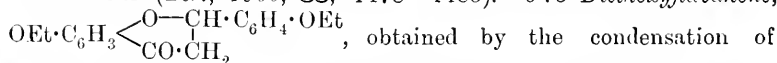
formula  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} : \text{C}_6\text{H}_2\text{O}(\text{OH})_2 \\ \text{CO} - \text{C}_6\text{H}(\text{OH})_2 \end{array} \text{O}$ ; it gives a triacetate which is easily

reduced with zinc dust and acetic acid. Cerulin yields a pentacetate, but not a tetracetate as stated by Buchka (*loc. cit.*); its constitution

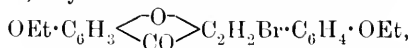


E. G.

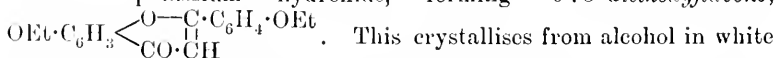
**6:3'-Dihydroxyflavone.** By J. BLUMSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, **33**, 1478—1483).—6:3'-*Diethoxyflavanone*,



*m*-ethoxybenzaldehyde with 2-hydroxy-5-ethoxyacetophenone under conditions previously described (compare this vol., i, 237, 238), crystallises from alcohol in colourless needles, melts at 96—97°, and has a blue fluorescence in alcoholic solution; with bromine in carbon disulphide solution, it yields the *monobromo*-derivative,



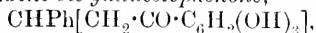
which crystallises from alcohol in white needles, melts at 112—113°, and loses hydrogen bromide when treated with warm concentrated alcoholic potassium hydroxide, forming 6:3'-*diethoxyflavone*,



leaflets, melts at 135—136°, shows a greenish fluorescence in sulphuric acid solution, and is resolved by heating with sodium in alcoholic solution, into 2-hydroxy-5-ethoxyacetophenone and *m*-ethoxybenzoic acid; when boiled for several hours with concentrated hydriodic acid, it yields 6:3'-*dihydroxyflavone*, which crystallises from alcohol in short, thick, colourless needles and melts at 300°; 6:3'-*diacetylflavone* crystallises from alcohol in white needles and melts at 169—170°.

Resacetophenone monoethyl ether (2 mols.) condenses with benzaldehyde in alcoholic solution under the influence of hydrogen chloride to form, not a flavanone, but *benzylidene-bis-resacetophenone monoethyl*

ether,  $\text{CHPh}[\text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OEt}]_2$ ,  $[\text{CO} : \text{OH} : \text{OEt} = 1 : 2 : 4]$ ; this crystallises from alcohol in slightly yellow needles, melts at  $211^\circ$ , and yields a *diacetate* which forms small, white needles and melts at  $138$ — $139^\circ$ . *Benzylidene-bis-gallacetophenone*,



obtained similarly, crystallises, with  $2\text{H}_2\text{O}$ , from dilute alcohol in beautiful rosettes of needles which lose their water of crystallisation when kept in a desiccator, and become opaque; it melts at  $226^\circ$ , and yields a *hexacetyl* derivative which crystallises from alcohol and melts at  $171$ — $172^\circ$ .

W. A. D.

**Oximes of some Flavonones.** By STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 1483—1484).—Although the flavones, like the xanthenes, are indifferent to hydroxylamine, the flavanones readily form oximes.

*6-Ethoxyflavanoneoxime*,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{O} \text{---} \text{CHPh} \\ \diagdown \quad \diagup \\ \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH}_2 \end{array}$ , crystallises from alcohol in white needles and melts at  $185$ — $186^\circ$ .

*4'-Methoxy-6-ethoxyflavanone*,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{O} \text{---} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \diagdown \quad \diagup \\ \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH}_2 \end{array}$ , crystallises from alcohol in white needles and melts at  $190$ — $191^\circ$ ; it is hydrolysed by boiling with alcoholic hydrochloric acid. The *acetate* crystallises from alcohol in white needles and melts at  $168^\circ$ .

T. M. L.

**7-Acetylamino- $\beta$ -naphthaquinone.** By FRIEDRICH KEHRMANN and H. WOLFF (*Ber.*, 1900, 33, 1538—1542).—*7-Acetylamino-2-naphthol*,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , obtained by shaking 7-amino-2-naphthol with acetic anhydride and a little dry sodium acetate, crystallises from alcohol in colourless, glistening plates melting at  $220^\circ$ ; on treatment with nitrous acid, it yields a *nitroso*-derivative, probably with the oxime constitution  $\text{NHAc} \cdot \text{C}_{10}\text{H}_5\text{O} : \text{N} \cdot \text{OH}$ ; this crystallises from benzene in yellowish-red, glistening plates decomposing at about  $220^\circ$ , and dissolves readily in boiling water, alcohol, or acetic acid. Dilute sulphuric acid precipitates it from its solution in alkalis as a dark red, crystalline precipitate which slowly changes to a pale yellow powder. When reduced with stannous chloride, the oxime yields *acetyldiamino-naphthol*,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{NH}_2$   $[\text{NH}_2 : \text{OH} : \text{NHAc} = 1 : 2 : 7]$ , in the form of its *hydrochloride*, together with a certain amount of diamino-naphthol hydrochloride, the *diacetyl* derivative of which crystallises in colourless needles melting at  $226^\circ$ .

*7-Acetylamino-1:2-naphthaquinone* crystallises from alcohol in glistening, almost black, needles, which rub down to a dark red powder; it melts and decomposes at about  $224^\circ$ , and is soluble in alcohol, acetic acid, or boiling water, yielding blood-red solutions. It differs from the isomeric compound previously described (*Abstr.*, 1899, i, 81) in its much deeper colour. When treated with amines, the hydrogen atom in position 4 is readily replaced by amino-groups.

*7-Acetylamino-4-anilino- $\beta$ -naphthaquinone*,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_4\text{O}_2 \cdot \text{NHPh}$ , forms small, brownish-red crystals, melts and decomposes at about  $280^\circ$ , and dissolves in alkalis, boiling alcohol, or acetic acid.

*9-Acetylaminonaphthaphenazine*,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_5 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$ , obtained by the condensation of *o*-phenylenediamine hydrochloride and 7-acetylaminonaphthaquinone in the presence of alcohol and a few drops of dilute sulphuric acid, crystallises from alcohol in yellow needles melting at  $288^\circ$ ; its alcoholic solution possesses a slight green fluorescence. When hydrolysed with sulphuric acid, it yields *9-aminonaphthaphenazine*, which crystallises from alcohol in glistening, reddish-brown needles melting at  $232^\circ$ , insoluble in water, and yielding mono-acid salts which have an olive-green colour. J. J. S.

**Preparation of Dialkylaminodichloroanthraquinones.** By ÉMILE C. SEVERIN (*Compt. rend.*, 1900, 130, 1405—1407).—*2'-Dimethylamino-3:4-dichlorobenzylbenzoic acid*, obtained by reduction of the corresponding benzoylbenzoic acid (this vol., i, 296), is a white solid which melts at  $233^\circ$  and becomes yellow when exposed to air (compare, however, this vol., i, 445). The corresponding *diethylamino-acid* crystallises in white needles melting at  $237^\circ$ . When heated with concentrated sulphuric acid at  $66^\circ$ , these acids yield respectively *2-dimethylamino-5:6-dichloroanthraquinone*, which crystallises in bronzed red needles melting at  $188^\circ$ , and the *diethylamino-compound*, which is similar in appearance, but melts at  $175^\circ$ . In this condensation, the benzylbenzoic acid is first converted into a ketohydroanthracene, which is subsequently oxidised by the excess of sulphuric acid.

The corresponding benzoylbenzoic acids, however, do not undergo similar condensation, which seems to be prevented by the presence of the two chlorine atoms in the 3 and 4 positions with respect to the carboxyl groups. C. H. B.

**New Homologues of Alizarin, Hystazarin, and Quinizarin.** By STEFAN VON NIEMENTOWSKI (*Ber.*, 1900, 33, 1629—1636).—When 4-methylphthalic anhydride is heated with catechol (1 mol.) and concentrated sulphuric acid for several hours at  $185^\circ$ , *2-methyl-6:7-hystazarin*,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH})_2$ , is formed together with a smaller proportion of the isomeric *methylalizarin*  $[(\text{OH})_2 : \text{Me} = 1:2:6 \text{ or } 1:2:7]$ . The latter crystallises from benzene, in which it is moderately soluble, in orange-red needles, melts at  $216^\circ$ , and can be sublimed; its tinctorial properties and absorption spectrum are similar to those of alizarin; its *diacetyl* derivative,  $\text{C}_{19}\text{H}_{14}\text{O}_6$ , crystallises from alcohol in stellar aggregates of bright yellow needles, and melts, with previous softening, at  $176^\circ$ . *2-Methyl-6:7-hystazarin* is almost insoluble in benzene, but separates from alcohol or glacial acetic acid in yellow crystals which melt and decompose between  $320^\circ$  and  $340^\circ$ , and, when distilled with zinc dust in a stream of hydrogen, yield 2-methylantracene; the *diacetate*,  $\text{C}_{19}\text{H}_{14}\text{O}_6$ , crystallises from alcohol in straw-coloured, felted needles and melts at  $208^\circ$ .

*2-Methyl-5:8-quinizarin*, prepared by heating quinol with 4-methylphthalic anhydride (1 mol.) and concentrated sulphuric acid for 5—10 hours at  $140$ — $160^\circ$ , crystallises from a mixture of alcohol and benzene in lustrous, orange-gold leaflets, and melts at  $165^\circ$ ; after fusion and resolidification, or after sublimation, however, it melts at  $175^\circ$ .



The *diacetyl* derivative crystallises from alcohol in yellow, obliquely truncated plates and melts at  $204^{\circ}$ ; attempts to prepare the corresponding dibenzoyl derivative failed. W. A. D.

**Bromine Derivatives of Quinizarin.** By CARL LIEBERMANN and C. N. RIIBER (*Ber.*, 1900, 33, 1658—1664).—*Bromoquinizarin*,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_6HBr(OH)_2$ , obtained when quinizarin is dissolved in 25 times its weight of glacial acetic acid and then boiled for 12 hours with 3 times its weight of bromine, forms a red, crystalline powder insoluble in all ordinary organic solvents, but soluble in alkali hydroxides, yielding blue or bluish-violet solutions. It sublimes at about  $300^{\circ}$  under reduced pressure and is deposited as ruby-red, glistening needles or plates.

*Dibromoquinizarin*,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_6Br_2(OH)_2$ , formed when quinizarin is heated with 6 times its weight of dry bromine in sealed tubes at  $100^{\circ}$  for 8 hours, sublimes at about  $350^{\circ}$  under reduced pressure, yielding red needles, and appears to form an unstable compound with bromine, which is, however, decomposed on exposure to the air. It is somewhat sparingly soluble in potassium hydroxide, yielding a deep blue solution, but is insoluble in cold sodium carbonate solution and in most organic solvents. The blue alkaline solution and the red solution in concentrated sulphuric acid exhibit two absorption bands almost identical with those given by similar solutions of quinizarin itself. When fused with potash, it yields purpurin and probably hydroxypurpurin which on oxidation are converted into phthalic acid.

A mixture of two isomeric *hexabromides*,  $C_{14}H_8O_4Br_6$ , is obtained when quinizarin is left in contact with some 40 times its weight of bromine for 3 days at  $0^{\circ}$ . The two may be separated by the aid of a moderate amount of carbon disulphide in which the one is insoluble; when the filtrate is cooled and mixed with its own volume of light petroleum, brownish-yellow crystals of the more soluble isomeride having the composition  $2C_{11}H_8O_4Br_6 \cdot CS_2$  are obtained. The less soluble compound forms canary yellow crystals, and when heated to  $210$ — $220^{\circ}$  melts and decomposes, yielding bromine, hydrogen bromide, and bromoquinizarin. It is insoluble in cold sodium carbonate and only sparingly soluble in ammonia, but more readily in potassium hydroxide, yielding a yellow solution.

The more soluble compound loses its carbon disulphide at  $70^{\circ}$  under reduced pressure and decomposes at  $175^{\circ}$  in much the same manner as its isomeride.

*Bromoquinizarin dibromide*,  $C_{11}H_7BrO_3Br_2$ , obtained by the action of an excess of bromine on quinizarin at  $40$ — $50^{\circ}$ , forms reddish-brown crystals decomposing at  $210^{\circ}$  and soluble in carbon disulphide, benzene, or acetic acid, but insoluble in cold alkalis. Bromoquinizarin appears to combine with 2 mols. of bromine at  $0^{\circ}$ , but this bromine is readily given up again at the ordinary temperature.

J. J. S.

Action of Hydrogen Bromide on Dextrorotatory Benzylidenecamphor, Bromobenzylcamphor and Dextrorotatory Benzylidenecampholic and Phenylhydroxyhomocampholic Acids. By ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1900, 130,

1362—1366).—*Bromobenzylcamphor*,  $C_8H_{14} \begin{matrix} \text{CH} \cdot \text{CHPhBr} \\ | \\ \text{CO} \end{matrix}$ , obtained

by the prolonged action of an acetic acid solution of hydrogen bromide on benzylidenecamphor, crystallises from ether or light petroleum in white granules which melt at  $146^\circ$ . In alcoholic solution, it has  $[\alpha]_D + 53.3^\circ$ . If the benzylidenecamphor is heated with the acid solution at  $100^\circ$  under pressure, or if the bromo-derivative just described is treated in the same way, *phenylhydroxyhomocampholic acid*,  $OH \cdot \text{CHPh} \cdot \text{CH}_2 \cdot C_8H_{14} \cdot \text{CO}_2H$ , is obtained, together with a small quantity of a viscous *benzylidenecampholic acid*,  $\text{CHPh} \cdot \text{CH} \cdot C_8H_{14} \cdot \text{CO}_2H$ . If the bromobenzylcamphor is treated with alcoholic potash, the second acid is the main product, and the first is formed in small quantity.

Phenylhydroxyhomocampholic acid melts at  $217^\circ$ , in alcoholic solution, has  $[\alpha]_D + 68.6^\circ$ , and crystallises with 1 mol. alcohol in transparent, efflorescent prisms. The methyl ester prepared from the silver salt melts at  $105^\circ$ , and when dissolved in toluene has  $[\alpha]_D + 66.4^\circ$ . When heated with methyl alcohol and hydrochloric acid, this acid yields the methyl ester of the benzylidenecampholic acid, which boils at  $205\text{--}210^\circ$  under 15 mm. pressure, and when dissolved in toluene has  $[\alpha]_D + 22^\circ$ .

The authors attribute to the influence of the double bond of the CHR group the readiness with which the benzylidene camphor combines with the elements of water, whilst the benzylidenecampholic acid is probably formed simply by the dehydration of the phenylhydroxyhomocampholic acid. The low rotatory power of benzylidenecampholic acid, as compared with that of benzylidenecamphor, is noteworthy, and indicates that a double bond on one of the branches of a broken camphor chain does not increase the rotatory power of the new product.

C. H. B.

Rhodinol and Citronellol. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 458—463).—The author briefly reviews the history of rhodinol and citronellol, replies to the criticisms of Tiemann and Schmidt (Abstr., 1896, i, 382), and maintains the accuracy of Barbier and Bouveault's views (Abstr., 1896, i, 446, 491, 492; 1897, i, 537) as to the constitution and distinct individuality of these compounds.

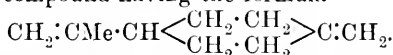
N. L.

Transformation of Rhodinal into Menthone. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 463—466).—A reply to Tiemann and Schmidt (Abstr., 1897, i, 199). Analyses are quoted in further proof of the isomeric change of rhodinal into menthone described by Barbier and Bouveault (Abstr., 1896, i, 491).

N. L.

Pseudo- and Ortho series of Terpenes, Terpene-alcohols, and Terpene-ketones. By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 1455—1467).—Terpene derivatives which contain a double bond between the nucleus and the side chain are termed by the author

*pseudo*-derivatives, the isomeric substances containing the double bond in the nucleus being denoted as *ortho*-derivatives; thus limonene,  $\text{CH}_2\text{:CMe}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\text{CMe}$ , would be an *ortho*-terpene, the corresponding *pseudo*-compound having the formula

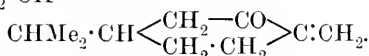


It is not improbable that dipentene has the latter formula, instead of being, as usually assumed, [*d* + *l*]-limonene; both substances would give rise to the same derivatives on interaction with halogen acids.

Orthopinene would be  $\text{CH}_2\begin{smallmatrix} \text{CH} \text{---} \text{CH}_2 \\ > \text{CMe}_2 \\ \text{CH} \text{---} \text{CMe} \end{smallmatrix}\text{CH}$ , and  $\psi$ -pinene

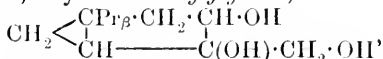
$\text{CH}_2\begin{smallmatrix} \text{CH} \text{---} \text{CH}_2 \\ > \text{CMe}_2 \\ \text{CH} \text{---} \text{CH}_2 \end{smallmatrix}\text{C:CH}_2$ ; orthocarvone would have the formula

$\text{CHMe}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CH} \end{smallmatrix}\text{CMe}$ , and  $\psi$ -carvone the formula

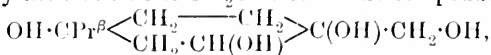


Sabinol, isolated by Fromm's method (Abstr., 1898, i, 674) from oil of savin, has a sp. gr. 0.9432 at 20°,  $\mu_D$  1.488, and a molecular refraction 46.5; from the following facts, it appears to be a  $\psi$ -terpene-alcohol,  $\text{CH}_2\begin{smallmatrix} \text{CPr}^\beta\cdot\text{CH}_2\cdot\text{CH}\cdot\text{OH} \\ \text{CH} \text{---} \text{C:CH}_2 \end{smallmatrix}$ . It is not a tertiary alcohol, since

it does not lose oxygen when heated with zinc dust (compare Abstr., 1894, i, 611; and this vol., i, 351), and because of the shape of the curves obtained by molecular weight determinations; it is not a primary alcohol, since it fails to interact with phthalic anhydride (compare Stephan, Abstr., 1899, i, 921). Hence, by exclusion, it is a secondary alcohol, although attempts to oxidise it to the corresponding ketone,  $\text{C}_{10}\text{H}_{18}\text{O}$ , failed. When oxidised with aqueous potassium permanganate at 0°, it yields *sabinyglycerol*,



which crystallises from water, melts at 152–153°, and is converted, on warming with water containing a trace of acid, into cuminyl alcohol; this occurs by the addition of  $\text{H}_2\text{O}$  to form the compound



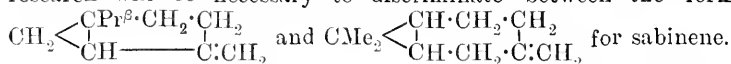
and the subsequent loss of  $2\text{H}_2\text{O}$ . When further oxidised by potassium permanganate, sabinol yields tanacetonedicarboxylic acid,  $\text{CH}_2\begin{smallmatrix} \text{CPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{CH}\cdot\text{CO}_2\text{H} \end{smallmatrix}$  (compare this vol., i, 240); on reduction with

sodium and amyl alcohol, it gives rise to tanacetyl alcohol,  $\text{C}_{10}\text{H}_{18}\text{O}$ , which is readily oxidised to tanacetone, characterised by its oxime (m. p. 52°). Sabinol is also converted into tanacetone by distilling with zinc dust, and, when warmed with absolute alcohol containing a few drops of sulphuric acid, yields cymene.

When oil of savin is distilled, a fraction, forming 30 per cent. of

the whole, boils between  $162^{\circ}$  and  $170^{\circ}$ , and consists principally of a terpene,  $C_{10}H_{16}$ , which the author terms *sabinene*; this has a sp. gr. 0.84,  $\mu_D$  1.466, a molecular refraction 44.9, and yields an oily *di-bromide* of sp. gr. 1.50. With ice-cold, aqueous potassium permanganate, sabinene yields a *glycol*,  $C_{10}H_{18}O_2$ , which boils at  $148-150^{\circ}$  under 15 mm. pressure, crystallises from water, melts at  $54^{\circ}$ , and has a sp. gr. 1.021,  $\mu_D$  1.402, and a molecular refraction 47.41, the calculated value being 47.97; on warming with acidified water, the glycol yields a *dihydrocuminyl alcohol*,  $C_{10}H_{16}O$ , which boils at  $242^{\circ}$ , has a sp. gr. 0.9572,  $\mu_D$  1.5018, a molecular refraction 46.80 (that calculated for 2 ethylenoid linkings being 46.76), and is oxidised by chromic acid to cuminyl alcohol and cuminaldehyde. These facts indicate that one of the hydroxyl groups of the glycol is in the nucleus, and that in sabinene, as in sabinol, there is a double-bond from the nucleus to a methylene group. *Sabinenic acid*,  $C_{10}H_{16}O_3$ , formed along with the foregoing glycol, crystallises from water, melts at  $57^{\circ}$ , and yields a sparingly soluble, crystalline *sodium* salt; it is an  $\alpha$ -hydroxy-acid, since it loses carbon dioxide when oxidised by lead peroxide to form *sabinene ketone*,  $C_9H_{14}O$ , which boils at  $213^{\circ}$ , has a sp. gr. 0.945,  $\mu_D$  1.4629, a molecular refraction 40.26 (that calculated for a ketone,  $C_9H_{14}O$ , without a double linking being 39.51), and yields a *semi-carbazone* crystallising from alcohol and melting at  $135-137^{\circ}$ . The ketone is levorotatory ( $\alpha_D$  in a 10 mm. tube =  $-18^{\circ}$ ), although sabinene, sabineneglycol, and sabinenic acid are all dextrorotatory.

On distilling sabinenic acid in a vacuum, water and hydrogen are eliminated and cumic acid formed (m. p.  $117-118^{\circ}$ ). Additional research will be necessary to discriminate between the formulae



W. A. D.

**Essential Oil of Jasmine Blossom. IV.** By ALBERT HESSE (*Ber.*, 1900, 33, 1585—1591. Compare Abstr., 1899, i, 376 and 441; and 1900, i, 48).—The investigation has been extended to the 'jasmine pur' obtained by extracting the blossom with a volatile solvent; of this, only about 25 per cent. is volatile with steam, and 5600 kilograms of blossom are therefore required to produce 1 kilogram of volatile oil. Where the oil is extracted from the blossoms by cold fat, only about 1000 kilograms are required, and the conclusion is therefore drawn that the blossoms only contain a small proportion of the oil ready formed, but steadily produce it during the 'enfleurage.' The oil differs in sp. gr. and in the proportion of ester from that obtained by 'enfleurage,' showing that the composition changes steadily after the blossoms are plucked.

'Jasmine pur' contains no methyl anthranilate, and therefore is not fluorescent. Jasmine is present, although the quantity was not sufficient for isolation, but there is not the slightest trace of indole, and this is therefore entirely absent in the blossoms, and is only produced during the 'enfleurage.'

T. M. L.

**Precipitation of Dyes by Ammonium Persulphate.** By FR. PRÖSCHER (*Chem. Zeit.*, 1900, 24, 262).—The following dyes are

quantitatively precipitated by the aid of ammonium persulphate: resorcinol-orange, neutral red, diethyltoluthionin chloride, succinicin-rhodamine, nitropentamethyl-violet, acridine-orange, and induline-scarlet; and the following almost completely: tetraethylsaffranine, Nile-blue; diethylsaffranine, thioflavine, rosinduline sulphate, pheno-saffranine, chrysaniline, naphthol-blue, and thionine. The fact that the dyes are not oxidised may be due to their quinonoid structure. Methylene-green is, however, readily oxidised. J. J. S.

**Leucomethylene-Blue.** By GEORG COHN (*Ber.*, 1900, 33, 1567—1568).—Leucomethylene-blue is so unstable that the preparation of acyl derivatives is a matter of great difficulty. Its compound with zinc chloride, on the other hand, readily yields acyl derivatives when treated with an acyl chloride or anhydride in presence of pyridine. *Benzoyl-leucomethylene-blue* forms colourless crystals melting at 185—187°, and is stable in the air; its *picrate* melts at 178°. When treated with ferric chloride, it gives first a green coloration and then a precipitate of the blue colouring matter. *Anisyl-leucomethylene-blue* melts at 106—107°, and *propionyl-leucomethylene-blue* at 145—146°; *butyryl-leucomethylene-blue* is a yellowish, crystalline powder melting at 143°, and *valeryl-leucomethylene-blue* melts at 155—156°.

The compound with stannic chloride may be employed in a similar manner, and analogous compounds can be prepared from ethylene-blue and "new methylene-blue." A. L.

**New Colouring Matters of Acid Function.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1900, [iii], 23, 456—457).—The simultaneous methylation and sulphonation of amino-groups in certain colouring matters, leuco-bases, and chromogens may be brought about by heating with a mixture of sodium hydrogen sulphite and formaldehyde in acid solution. The application of this process to magenta, *p*-nitrodianinotriphenylmethane, thionine, saffranine, and the nitranilines is referred to in the paper. N. L.

**New Blue Colouring Matter, Fast to Alkalis.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1900, [iii], 23, 457—458).—The action of formaldehyde and sodium hydrogen sulphite (see preceding abstract) on tetranethyltriaminodiphenyltolylmethane leads to the formation of a blue colouring matter in which the group  $\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$  stands in the *ortho*-position with respect to the central carbon atom; it resembles the similar *ortho*-sulphonated compounds prepared by Suais and Sandmeyer in resisting the action of alkalis. N. L.

**Brilliant Fast Red G.** By E. KOHNER (*J. pr. Chem.*, 1900, [ii], 61, 228—232).—"Brilliant fast red G" can be synthetically prepared by diazotising  $\alpha$ -naphthylamine-5-sulphonic acid and subsequent treatment with  $\beta$ -naphthol.

$\alpha$ -Naphthylamine-5-sulphonic acid is the only  $\alpha$ -naphthylaminesulphonic acid which gives a violet-red coloration with bromine water.

R. H. P.

**Pilocarpine.** By ADOLF PINNER and E. KOHLHAMMER (*Ber.*, 1900, 33, 1424—1431. Compare Jowett, *Trans.*, 1900, 77, 494, 851).—The observations of Hardy and Calmels (*Abstr.*, 1886, 724, 900, 1048; 1887, 1057) seem quite erroneous. No pyridinelactic acid could be obtained by prolonged boiling of pilocarpine with water or aqueous barium hydroxide; the alkali remained unchanged. Nor was it possible to obtain pyridinetartronic acid by oxidising pilocarpine with potassium permanganate; indeed, it seems possible that the product may be an acid free from nitrogen.

When pilocarpine is treated with three times its weight of bromine, 80 per cent. acetic acid being used as the solvent, yellowish-red needles of a perbromide,  $C_{11}H_{14}O_2N_2Br_2 \cdot HBr \cdot Br_2$ , are obtained; these melt at  $106^\circ$  (compare Chastaing, *Abstr.*, 1884, 468); the substance is not affected by water in the cold, however. When the perbromide is treated with dilute ammonia, dibromopilocarpine,  $C_{11}H_{14}O_2N_2Br_2$ , is formed; this was obtained crystalline and melted at  $79^\circ$ . By heating pilocarpine,  $C_{11}H_{16}O_2N_2$ , with bromine and water at  $100^\circ$ , *bromocarpic acid*,  $C_{10}H_{15}O_4N_2Br$ , is formed, along with another acid; evidently, the reaction is in a greater degree one of oxidation than of substitution. Bromocarpic acid melts at  $194^\circ$ ; its *barium* salt has the composition  $C_{10}H_{13}O_4N_2BrBa \cdot 5H_2O$ ; when heated with strong aqueous barium hydroxide for 12 hours at  $160$ — $180^\circ$ , the acid is for the most part entirely decomposed, and 78 per cent. of its nitrogen is obtained in the form of ammonia and methylamine. When pilocarpine is oxidised with permanganate, only 5 atoms of the latter per mol. of the alkaloid are taken up in the cold; probably, therefore, the bromine first oxidises the pilocarpine to a hydroxycarpic acid,  $C_{11}H_{16}O_2N_2 + 5O = CO_2 + C_{10}H_{16}O_5N_2$ , of which the hydroxyl group is then replaced by bromine through the agency of the hydrobromic acid formed in the first reaction. C. F. B.

**Pyridine Series. II.** By WILHELM MARCKWALD, W. KLEMM, and H. TRABERT (*Ber.*, 1900, 33, 1556—1566. Compare *Abstr.*, 1894, i, 381).—2-Pyridyl mercaptan,  $C_5NH_4 \cdot SH$ , is formed by the action of potassium hydrosulphide on 2-chloropyridine, and crystallises in almost odourless, yellow prisms melting at  $125^\circ$ . Solutions of this substance in indifferent solvents and in dilute acids are yellow, whilst solutions in alkalis and strong acids are colourless. This is probably due to the fact that the substance is tautomeric, existing in the yellow form as a thiopyridone,  $NH \langle \begin{smallmatrix} CH:CH \\ CS-CH \end{smallmatrix} \rangle CH$ , whilst the colourless solutions contain salts of the true mercaptan. The cuprous salt is a reddish-yellow powder. Methyl iodide converts the mercaptan into pyridyl 2-methosulphide,  $C_5NH_4 \cdot SMe$ , which is a colourless oil boiling at  $197^\circ$ , and possessing a characteristic odour. The hydrochloride forms white crystals, the hydriodide melts at  $155$ — $157^\circ$ , the platinichloride at  $185$ — $187^\circ$ , and the picrate at  $155^\circ$ . This sulphide is converted by oxidation into pyridyl-2-methylsulphone,  $C_5NH_4 \cdot SO_2Me$ , which is a thick oil boiling with partial decomposition at about  $325^\circ$ ; it has only very feebly basic properties, and forms a mercurichloride,  $(C_5H_7O_2NS)_2HgCl_2$ , which melts at  $125^\circ$ . Pyridyl-2-thioglycollic

*acid*,  $C_5NH_4 \cdot S \cdot CH_2 \cdot CO_2H$ , is obtained by the action of chloroacetic acid on the mercaptan, and forms yellowish crystals melting at  $127^\circ$ . The *hydrochloride* also forms yellowish crystals and melts at  $166-167^\circ$ .

2-Pyridyl sulphide is not formed by the action of potassium sulphide on chloropyridine, pyridylmercaptan being the sole product. 2-Pyridyl disulphide,  $C_5NH_4 \cdot S \cdot S \cdot C_5H_4N$ , obtained by the action of iodine on the mercaptan, crystallises in needles melting at  $57-58^\circ$ , and is only a weak monacid base. The *platinichloride* melts at  $150^\circ$ , and the *picrate* at  $119^\circ$ . Pyridine-2-sulphonic acid,  $C_5H_4N \cdot SO_3H$ , is produced by the action of dilute nitric acid on the mercaptan, and crystallises in needles melting at  $239-240^\circ$ . The *barium* salt is readily soluble, and the *silver* salt sparingly so in water.

2:6-Lutidyl 4-mercaptan,  $C_8NH_5Me_2 \cdot SH$ , forms yellow crystals melting at  $224^\circ$ , and yields colourless solutions in both acids and alkalis, which probably contain salts of the tautomeric thiolutidone,  $C_8NH_3Me_2 \cdot S$ . The compounds with acids are stable; the *hydrochloride* forms white crystals which melt at  $258^\circ$ , and the *picrate* melts at  $179^\circ$ . 2:6-Lutidyl 4-methosulphide,  $C_7H_8N \cdot SMe$ , melts at  $51^\circ$ , boils at  $233^\circ$ , and crystallises from water with  $3H_2O$ . The *hydriodide* melts at  $224-225^\circ$ , the *dichromate* melts and decomposes at  $160^\circ$ , and the *platinichloride* at  $245^\circ$ , whilst the *picrate* melts at  $169^\circ$ .

2:6-Lutidyl-4-methylsulphone crystallises in long, white, silky needles, and is a well-marked base. The *platinichloride* melts and decomposes at  $226^\circ$ , the *dichromate* at  $119^\circ$ , and the *picrate* at  $221^\circ$ .

Lutidyl acetonyl sulphide,  $C_7NH_8 \cdot S \cdot CH_2 \cdot COMe$ , is obtained by the action of chloroacetone on the mercaptan, and crystallises in lustrous white needles melting at  $83-84^\circ$ . The *hydrochloride* melts and decomposes at  $225^\circ$ , the *platinichloride* melts at  $126-127^\circ$ , and the *picrate* at  $181-182^\circ$ . The *oxime* forms white crystals melting at  $122-123^\circ$ .

2:6-Lutidyl 4-sulphide,  $(C_7H_8N)_2S$ , is readily formed by the action of potassium sulphide on chlorolutidine and melts at  $82-83^\circ$ ; it is a diacid base, the *platinichloride* melting at  $268^\circ$ , and the *picrate* at  $206-207^\circ$ , whilst the *dichromate* decomposes explosively at  $180^\circ$ . Di-2:6-lutidyl-4-sulphone,  $SO_2(C_7H_8N)_2$ , forms long, white needles melting at  $114^\circ$ , and is a diacid base. The *nitrate* can be recrystallised from alcohol, and decomposes at  $175^\circ$ ; the *platinichloride* melts and decomposes at  $262^\circ$ , the *dichromate* at  $185^\circ$ , and the *picrate* also at  $185^\circ$ . The *monopicrate* melts at  $193-194^\circ$ . 2:6-Lutidyl 4-disulphide,  $C_7H_8N \cdot S \cdot S \cdot C_7H_8N$ , forms white crystals melting at  $57^\circ$ , and is a diacid base. The *platinichloride*, *picrate*, and *dichromate* decompose when heated without melting. The disulphide is also produced by the oxidation of the mercaptan with nitric acid, potassium permanganate, and, quantitatively, with hydrogen peroxide in neutral solution; it is very readily reduced to the mercaptan. Hydrogen peroxide, on the other hand, in alkaline solution, converts the mercaptan into 2:6-lutidyl-4-sulphonic acid,  $C_7H_8N \cdot SO_3H$ , which forms white crystals, and is unaffected by being heated to  $300^\circ$ . The *barium* salt is readily soluble, and the *silver* salt sparingly so in water.

**Action of Hypochlorous Acid on Tertiary Amines.** By RICHARD WILLSTÄTTER and FRITZ IGLAUER (*Ber.*, 1900, 33, 1636—1641).—Hypochlorous acid interacts vigorously with tertiary amines to form a dialkyl nitrogen chloride (iminochloride) by the elimination of an alkyl radicle, thus:  $\text{NR}^1\text{R}^2\text{R}^3 + \text{HClO} = \text{NR}^1\text{R}^2\text{R}^3\text{Cl} + \text{R}^1\text{OH}$ ; it is possible that the additive compound,  $\text{NR}^1\text{R}^2\text{R}^3\text{Cl}(\text{OH})$ , is initially formed in this action, although, in view of the stability of compounds of the latter type (the hydrochlorides of the dialkylamine oxides, compare especially Bamberger and Tschirner, *Abstr.*, 1899, i, 347) this appears hardly probable.

*Chloronortropidine*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{NCl} \quad \text{CH} \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array}$ , is formed on adding tropidine to

an aqueous solution of hypochlorous acid (compare Einhorn, *Abstr.*, 1890, 90); the yield is good. It boils at  $79-80^\circ$  under 15 mm. pressure, has a pungent, irritating odour, is volatile with steam, and slowly decomposes on keeping. It has the properties of a weak base, since it dissolves in dilute mineral acids, and is recovered unchanged on adding ammonium sulphate; it is easily reduced by zinc dust and water or aqueous sodium hydrogen sulphite to *nortropidine*,

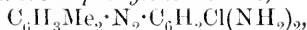
$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{NH} \quad \text{CH} \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array}$ , which boils at  $160^\circ$  (corr.), is miscible with hot water,

and yields a crystalline *carbonate*, a well defined *nitrosoamine*, a sparingly soluble *picrate*, and a beautifully crystalline *platinichloride*.

Hypochlorous acid converts tropane into an iminochloride which on reduction yields nortropan (norhydrotropidine), whilst with N-methylpiperidine, piperylene nitrogen chloride (Bally, *Abstr.*, 1888, 964; Lellman and Geller, *ibid.*, 970) is obtained. W. A. D.

**4-Chloro-*m*-phenylenediamine.** By PAUL COHN and ARMIN FISCHER (*Monatsh.*, 1900, 21, 267—279).—4-Chloro-*m*-phenylenediamine, prepared by reduction of 4-chloro-*m*-dinitrobenzene, crystallises in the rhombic system [ $a : b : c = 1 : 0.7106 : 0.6375$ ], is easily soluble in alcohol, chloroform, or hot water, and melts at  $91^\circ$ , not  $86^\circ$  as stated by Beilstein and Kurbatoff (*Abstr.*, 1879, 144). The aqueous solution reduces silver nitrate solution and is rapidly oxidised by ferric chloride or potassium dichromate, a property which characterises the salts which for the most part are crystalline, colourless, soluble in water, and insoluble in organic solvents. The following were prepared: the *hydrochloride*, which decomposes at  $205^\circ$ , the *platinichloride*, *sulphate*, *oxalate*, and *tartrate*. The *acetyl* derivative melts at  $170^\circ$  and the *dibenzoyl* derivative at  $178^\circ$ .

*as-m-Xyleneazo-4-chloro-m-phenylenediamine*,



prepared by treating the chlorophenylenediamine with diazotised *as*-m-xylidine crystallises in fine, reddish-yellow needles, easily soluble in organic solvents and sparingly in water, and melts at  $150^\circ$ .

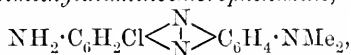
*p-Tolueneazo-4-chloro-m-phenylenediamine*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_2\text{Cl}(\text{NH}_2)_2$ , prepared in an analogous manner, crystallises in fine, orange-red



leaflets, is soluble in hot water and organic solvents, and melts at  $172^{\circ}$ .

*Benzeneazobenzene-4-chloro-m-phenylenediamine*,  $N_2Ph \cdot C_6H_4Cl(NH_2)_2$ , made by the action of diazobenzene chloride, forms lustrous, orange-red leaflets, is soluble in organic solvents and hot water, and melts at  $151^{\circ}$ .

The eurhodine, *dimethyldiaminochlorophenazine*,



prepared by the action of *p*-nitrosodimethylaniline, is easily soluble in alcohol and water, and gives with acids the colour reactions characteristic of this class of compounds.

1:2:4-Trichlorobenzene was prepared by Sandmeyer's reaction. 1-Nitro-2:4:5-trichlorobenzene melts at  $55^{\circ}$ , not  $57^{\circ}$ , as stated.

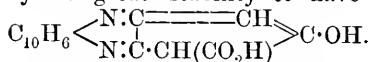
R. L. J.

**Condensation of Ethyl Cetipate with *o*-Diamines. I. Condensation with Ethylenediamine and the Naphthylene-*o*-diamines.** By RENÉ THOMAS-MAMERT and ST. WEIL (*Bull. Soc. Chim.*, 1900, [iii], 23, 438—456).—The condensation products of ethyl cetipate (oxalldiacetate) with diamines are characterised by the facility with which the adjacent  $CH_2 \cdot CO_2Et$  groups interact to form a pentatomic closed chain. The nucleus,  $C_6H_4 \begin{array}{c} \text{N} : C \cdot CH_2 \\ | \\ \text{N} : C \cdot CH_2 \end{array} > CO$ , which is contained in many of the compounds described, is designated phenoketopentamethylenazine.

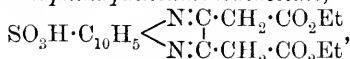
*Ethyl dihydropyrazine-2:3-diacetate*,  $C_4N_2H_4(CH_2 \cdot CO_2Et)_2$ , obtained by gently warming ethylenediamine with an alcoholic solution of ethyl cetipate, crystallises in large, yellow needles melting at  $100^{\circ}$ , and is hydrolysed by concentrated hydrochloric acid to the *hydrochloride*,  $\begin{array}{c} CH_2 \cdot N \\ | \\ CH_2 \cdot N(HCl) \end{array} \begin{array}{c} \text{N} : C \cdot CH_2 \\ | \\ \text{N} : C \cdot CH_2 \end{array} > CO$ , which crystallises in microscopic, green needles.

*Ethyl 1:2-naphthaquinoxalinediacetate*,  $C_{10}H_6 \begin{array}{c} \text{N} : C \cdot CH_2 \cdot CO_2Et \\ | \\ \text{N} : C \cdot CH_2 \cdot CO_2Et \end{array} > CO$ , from ethyl cetipate and 1:2-naphthylenediamine, crystallises in highly refractive, brownish-yellow needles melting at  $98^{\circ}$ , and is converted by the action of alcoholic potash into the corresponding *potassium salt*, which crystallises well. This, when heated with dilute sulphuric acid, yields (1) the dibasic acid,  $C_{10}H_6 \begin{array}{c} \text{N} : C \cdot CH_2 \cdot CO_2H \\ | \\ \text{N} : C \cdot CH_2 \cdot CO_2H \end{array} > CO$ , which, however, was not isolated; (2) 1:2-naphtha- $\beta$ -ketopentamethylenazinecarboxylic acid,  $C_{10}H_6 \begin{array}{c} \text{N} : C \cdot CH_2 \\ | \\ \text{N} : C \cdot CH(CO_2H) \end{array} > CO$ , which crystallises in slender, yellow needles decomposing, without melting, at  $190^{\circ}$ ; (3) naphtha-ketopentamethylenazine, which was separated by means of its *bromine derivative*,  $C_{10}H_6 \begin{array}{c} \text{N} : C \cdot CHBr \\ | \\ \text{N} : C \cdot CH_2 \end{array} > CO$ , crystallising in yellow needles which remain unmelted at  $275^{\circ}$ , and its *sulphate*,  $C_{15}H_{10}ON_2H_2SO_4$ , which crystallises in brown needles and decomposes, without melting, above  $262^{\circ}$ .

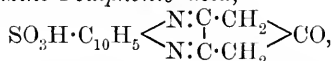
*Ethyl 1:2-naphtha-β-ketopentamethylenazinecarboxylate*, obtained by the action of sodium ethoxide on ethyl 1:2-naphthaquinoxalinediacetate, crystallises in large, golden-yellow, silky needles which decompose, without melting, at about 250°; its solution in chloroform has a magnificent green fluorescence, whilst its solution in concentrated sulphuric acid is of a blood-red colour. The corresponding *acid* crystallises in yellow needles which decompose at 190°, and is shown by its great stability to have most probably the enolic formula,



*Ethyl 4-sulpho-1:2-naphthaquinoxalinediacetate*,



obtained by treating ethyl cetipate with 1:2-naphthylenediamine-4-sulphonic acid in acetic acid solution, crystallises in greenish-yellow, microscopic needles which remain unaltered at 285°. The corresponding *acid* crystallises in brown needles, which are unaltered by heating at 275°, and is converted by boiling with water into 1:2-naphtha-β-ketopentamethylenazine-4-sulphonic acid,



which crystallises with 1H<sub>2</sub>O and is unaltered by heating at 230°.

*Ethyl 2:3-naphthaquinoxalinediacetate*, formed by the action of 2:3-naphthylenediamine on ethyl cetipate, crystallises in orange, cauliflower-like masses melting at 139.5°. The analysis of this compound presented considerable difficulties on account of the slowness with which it undergoes combustion. In this respect, it was found to resemble *o*-diphenyl-2:3-naphthaquinoxaline, obtained in an analogous manner from benzil and 2:3-naphthylenediamine, which forms microscopic, yellow crystals melting at 189.5–190°. When treated successively with sodium ethoxide and sulphuric acid, ethyl 2:3-naphthaquinoxalinediacetate yields the *sulphate of ethyl 2:3-naphtha-β keto-pentamethylenazinecarboxylate*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N}:\text{C}\cdot\text{CH}(\text{CO}_2\text{Et}) \\ | \\ \text{N}:\text{C}\text{---}\text{CH}_2 \end{array} \text{CO}$ , a dark

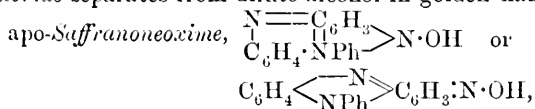
yellow powder which decomposes, without melting, at about 200°.

N. L.

**Saffranine and Rosinduline.** By OTTO FISCHER and EDUARD HEPP [with FRIED. LINNEMANN, ALEXANDER GUTBIER, and WALTHER DILTHEY] (*Ber.*, 1900, 33, 1485–1498. Compare Abstr., 1898, i, 334). —*apo-Saffranine hydrobromide*,  $\text{C}_{18}\text{H}_{14}\text{N}_3\text{Br}$ , crystallises from alcohol in dark red prisms with a green lustre. *apo-Saffranone chlorobromide* (chlorophenylphenazonium bromide),  $\text{C}_6\text{H}_5\text{Cl} \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPhBr} \end{array} \text{C}_6\text{H}_4$ , crystallises from methyl alcohol in brownish-red, glistening flakes. *apo-Saffranone platinumchloride*,  $(\text{C}_{18}\text{H}_{12}\text{N}_2\text{Cl})_2\cdot\text{PtCl}_6$ , separates from dilute alcohol in dark reddish-brown needles with a blue lustre; the *auri-chloride*,  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{ClAuCl}_4\cdot\text{H}_2\text{O}$ , forms long needles with a blue lustre.

*p-Tolylaposafranine bromide*,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPhBr} \end{array} \text{C}_6\text{H}_4$ , prepared by the action of *p*-toluidine on *aposafranine* bromide, separates

from dilute alcohol in bronze-like needles; the *base* crystallises from a mixture of alcohol and benzene, and melts at  $196^{\circ}$ ; the *platinichloride* separates from dilute alcohol in golden flakes.



prepared by the action of hydroxylamine hydrochloride on *apo-saffranone* in presence of concentrated potassium hydroxide solution, is insoluble in water, crystallises from dilute alcohol, has a very high melting point, forms salts with strong acids, and resembles *apo-saffranone* in giving a dichroic solution in sulphuric acid. The basic *aurichloride*,  $(\text{C}_{15}\text{H}_{13}\text{N}_3\text{O})_2 \cdot \text{HAuCl}_4$ , forms dark green, glistening crystals.

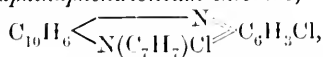
*iso-Rosindoneoxime*,  $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{NPh} \end{array} \text{N} \cdot \text{OH}$ , prepared in a similar way from *isorosindone*, crystallises from dilute alcohol in greenish, lustrous prisms; the *hydrochloride* crystallises in bluish needles.

*7-Ethylisorosindoneoxime*,  $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{NEt} \end{array} \text{N} \cdot \text{OH}$ , resembles the preceding compound; the *hydrochloride* crystallises in bluish, lustrous needles.

*7-o-Tolylisorosindone*,  $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{N}(\text{C}_7\text{H}_7) \end{array} \text{O}$ , prepared by condensing *p* nitrophenol with *o*-tolyl- $\beta$ -naphthylamine, crystallises from alcohol in dark red needles, melts at  $148^{\circ}$ , and closely resembles *rosindone*. The *hydrochloride* crystallises from dilute hydrochloric acid in orange-red flakes. The less soluble *hydrobromide* forms green, glistening crystals. The *aurichloride* forms dark red, glistening needles.

*7-o-Tolylrosindoneoxime*,  $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{N}(\text{C}_7\text{H}_7) \end{array} \text{N} \cdot \text{OH}$ , forms a resinous mass with a green shimmer. The *hydrochloride* crystallises from a mixture of alcohol and ether in glistening prisms. The basic *aurichloride*,  $(\text{C}_{23}\text{H}_{17}\text{N}_3\text{O})_2 \cdot \text{HAuCl}_4$ , crystallises from water in well-formed, green, glistening needles.

*7-Chloro-7 o tolylnaphthaphenazonium chloride*,

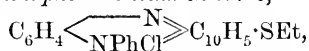


prepared by the action of phosphorus pentachloride on the indone, separates from a mixture of alcohol and ether in stout, yellowish-brown crystals with a blue shimmer. The *hydrochloride* is readily soluble in alcohol and in water, and reacts with bases in the same way as *isorosindone chloride*. The *platinichloride*,  $(\text{C}_{23}\text{H}_{16}\text{N}_2\text{Cl})_2 \cdot \text{PtCl}_6$ , forms long, orange-yellow tablets. The *aurichloride*,  $\text{C}_{23}\text{H}_{16}\text{N}_2\text{ClAuCl}_4$ , crystallises from dilute alcohol or from water in yellowish-brown, golden-glistening flakes.

*Thiorosindone*,  $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_4 \cdot \text{NPh} \end{array} \text{S}$ , prepared by the action of potassium hydrosulphide on the chloride, crystallises from pyridine in dark blue

flakes with a metallic lustre, is insoluble in water, and only slightly soluble in organic solvents; it is hydrolysed only slowly by heating with concentrated hydrochloric acid under pressure.

*Ethylthiophenyl-naphthaphenazonium chloride*,

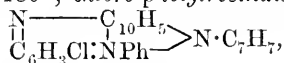


prepared by the action of mercury mercaptide on rosindone chloride, crystallises from alcohol in glistening, brown needles.

*iso-Rosindine chloride*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPhCl} \end{array} \text{C}_6\text{H}_3\text{Cl}$ , crystallises from absolute alcohol in yellowish-red, green-glistening needles. The *ferrichloride* crystallises from alcohol in yellow needles, the *mercurichloride* forms yellowish-red needles, and the *thiocyanate* crystallises in brown needles. Unlike rosindone chloride, *isorosindone chloride* is not readily hydrolysed; on heating with water, it is converted into *isorosindone* together with a small amount of *chloro-rosindone*,  $\text{C}_6\text{H}_3\text{Cl} \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPh} \end{array} \text{C}_{10}\text{H}_5 \cdot \text{O}$ ; this is formed in larger quantities on heating *isorosindone chloride* with alkalis, sodium acetate, or sodium phosphate, crystallises from benzene in glistening needles, and melts at  $268^\circ$ .

Whilst *isorosindone chloride* interacts with aniline in alcoholic solution to form phenyl*isorosinduline chloride*, in aqueous solution it gives chiefly chlorophenylrosinduline, identical with that prepared by Kehrmann from anilino- $\beta$ -naphthaquinone and chlorophenyl-*o*-phenylenediamine. Similar products are obtained with *p*-toluidine;

*p* *tolylosorosinduline nitrate*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPh}(\text{NO}_3) \end{array} \text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , forms steel-blue, glistening needles, whilst the *base* forms violet, glistening tablets, and melts at  $186^\circ$ ; *chloro-p-tolylosinduline*,



crystallises from a mixture of alcohol and benzene in black flakes, melts at  $215\text{--}216^\circ$ , and forms a difficultly soluble, red *sulphate*.

Naphthindone is converted by the action of phosphorus pentachloride into 7-chloro-7-phenyl-naphthazonium chloride,  $\text{C}_{10}\text{H}_5 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPhCl} \end{array} \text{C}_{10}\text{H}_5\text{Cl}$ ; this crystallises from a mixture of alcohol and ether in reddish-yellow, green-glistening needles, and gives a crystalline *platinichloride*, *ferrichloride*, and *mercurichloride*.  
T. M. L.

**Constitution of the Induline of the Aminoazobenzene Fusion.** By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1900, 33, 1498—1503).—The blue induline,  $\text{C}_{30}\text{H}_{23}\text{N}_5$ , of the amidoazobenzene fusion (Fischer and Hepp, *Abstr.*, 1896, i, 50 and 323) is now shown

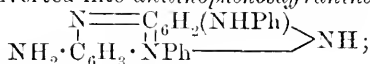
to have the structure  $\begin{array}{c} \text{N} \\ \text{---} \\ \text{C}_{16}\text{H}_2(\text{NHPh}) \\ \text{---} \\ \text{N} \end{array} \begin{array}{c} 7 \\ \text{N} \end{array} \begin{array}{c} 2 \\ \text{C}_6\text{H}_3 \end{array} \begin{array}{c} 3 \\ \text{NPh} \end{array}$ , and is thus an anilinomauveine or anilinophenylphenosaffranine. The *hydrochloride*,  $\text{C}_{30}\text{H}_{24}\text{N}_5\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ , crystallises from alcohol in small, green,

glistening needles; the *hydrobromide*, bronze-like, lustrous needles; the *hydriodide*, green, glistening needles; the *sulphate*, glistening, prismatic crystals and the *picrate*, bronze-like flakes.

With nitrous acid, the induline gives a *diazo*-compound, which, when boiled with alcohol, gives an anilinophenylaposafranine,  $\text{N}=\text{C}_6\text{H}_2(\text{NHPh})\text{C}_6\text{H}_4\cdot\text{NPh} \longrightarrow \text{NPh}$ , which is identical with that obtained by the action of aniline and aniline hydrochloride on *aposafranine*, and can be hydrolysed to anilinoaposafranone and aniline, and further to hydroxyaposafranone and aniline.

The induline is hydrolysed by dilute sulphuric acid at 230–250° to dihydroxyaposafranone,  $\text{OH}\cdot\text{C}_6\text{H}_3\cdot\text{NPh} \xrightarrow{\text{N}=\text{C}_6\text{H}_2(\text{OH})\text{C}_6\text{H}_3\cdot\text{NPh}} \text{O}$ .

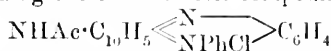
By heating with ammonia and ammonium chloride at 130–140°, the induline is converted into *anilinophenosaffranine*,



the base crystallises from pyridine in green prisms and melts and decomposes at 158°; it forms a soluble *acid sulphate* and a *neutral sulphate*,  $(\text{C}_{24}\text{H}_{19}\text{N}_5)_2\cdot\text{H}_2\text{SO}_4$ , which crystallises from dilute alcohol in glistening prisms; the *hydrochloride*,  $\text{C}_{24}\text{H}_{19}\text{N}_5\cdot\text{HCl}$ , forms violet needles with a metallic lustre. By the action of nitrous acid and alcohol, the amino-group is removed and the base is converted into anilinoaposafranine, identical with that prepared from *aposafranine* and aniline, and by the oxidation of *o*-aminodiphenylamine; the formation of this compound proves that the  $-\text{NPh}-$  group of the induline is in the ortho-position relatively to the  $-\text{NHPh}$  group. The anilinoaposafranine is converted by zinc dust and acetic acid into *aposafranine* and aniline.

T. M. L.

**The Tenth and Eleventh Isomerides of Rosinduline.** By FRIEDRICH KEHRMANN and H. WOLFF (*Ber.*, 1900, 33, 1543–1548. Compare *Abstr.*, 1898, i, 154, 155; 1899, i, 238, 525; this vol., i, 60). —7-Acetylamino-1:2-naphthaquinone (compare this vol., i, 449) readily condenses with an alcoholic solution of phenyl-*o*-phenylenediamine hydrochloride, yielding the two isomeric compounds,



(Ph in positions 7 and 12 respectively), which, when hydrolysed, yield the tenth and eleventh *isorosindulines*. The original condensation products are best isolated as their bromides by the addition of solid sodium bromide, and separated by the aid of a moderate quantity of hot water, in which the acetylamino-7-phenylnaphthaphenazonium bromide is almost insoluble.

**2-Acetylamino-12-phenylisonaphthaphenazonium 12 bromide**, which is formed in much the larger quantity, crystallises from alcohol in chocolate-coloured, glistening plates, and is readily soluble in hot water to a yellowish-brown solution, which does not exhibit fluorescence; its alcoholic solution is coloured violet-blue on the addition of dimethylamine. The *dichromate*,  $(\text{C}_{21}\text{H}_{18}\text{ON}_3)_2\text{Cr}_2\text{O}_7$ , forms black-brown crystals insoluble in water.

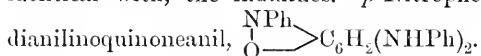
2-Amino-12-phenylisonaphthaphenazonium 12-bromide (isorosinduline No. 10) crystallises in long, black-green prisms, or in small, dark green nodular masses; it dissolves readily in water or alcohol, and its solutions exhibit no fluorescence. The *dichromate*,  $(C_{22}H_{16}N_3)_2Cr_2O_7$ , forms a dark green, crystalline precipitate insoluble in water.

2-Acetamino-7-phenylnaphthaphenazonium 7-bromide crystallises from boiling alcohol in dark brown plates with a bronzy lustre; its solutions have a cherry-red colour, but exhibit no fluorescence.

2-Amino-7-phenylnaphthaphenazonium bromide (isorosinduline No. 11) crystallises in black, glistening prisms, readily soluble in water to bluish-green solutions, and the *dichromate* forms a dark green, crystalline powder.

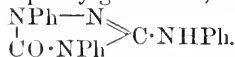
The constitutions of the two bromides were established by removing the amino-group; the isorosinduline No. 10 gave a phenylisonaphthaphenazonium salt, and the isomeric compound phenylnaphthaphenazonium. J. J. S.

Electrolytic Preparation of Colouring Matters Resembling Indulines. By WALTHER LÖB (*Zeit. Elektrochem.*, 1900, 6, 441).—A solution of 2 parts of aniline in 1 part of aqueous hydrochloric acid (sp. gr. 1.19) readily dissolves aromatic nitro-compounds. Such solutions, when reduced at the cathode of an electrolytic cell, yield colouring matters which resemble, though they are probably not identical with, the indulines. *p*-Nitrophenol gives a good yield of



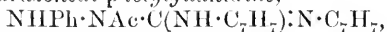
T. E.

Phenylhydrazone-carbo- and -dicarbo-diimine. The Decomposition Product of Wessel's Dicarbo-base. By CARL SCHALL (*J. pr. Chem.*, 1900, ii, 61, 440—448. Compare Abstr., 1893, i, 461; and Wessel, Abstr., 1888, 1083).—Wessel's base gives a dark yellow dinitroso-derivative,  $C_{32}H_{26}N_6(NO)_2$ , which melts and decomposes at  $112^\circ$ . The decomposition product,  $C_{20}H_{16}ON_3$  (Abstr., 1893, i, 461), has been prepared by the action of carbonyl chloride on anilino-diphenylguanidine, and is therefore regarded as having the formula



Phenylhydrazoncarbodi-*p*-tolylamine melts at  $168\text{--}170^\circ$  and not at  $138^\circ$  (Wessel, *loc. cit.*); it is readily oxidised by mercuric oxide to the *azo*-derivative,  $\text{NPh} \cdot \text{N} \cdot \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \cdot \text{N} \cdot \text{C}_7\text{H}_7$ , which forms deep-red needles and melts at  $115^\circ$ .

Acetylphenylhydrazonedi-*p*-tolylguanidine,



prepared from acetylphenylhydrazine and carbodi-*p*-tolylimide, crystallises from alcohol in white needles and melts at  $200^\circ$ . The *dibromo*-derivative,  $C_{23}H_{22}ON_4Br_2$ , melts at  $215^\circ$ ; the *nitro*-derivative,  $C_{21}H_{21}N_4 \cdot NO_2$ , which does not contain an acetyl group, is a dark-red compound, and melts at  $208^\circ$ .

T. M. L.

Electrolytic Reduction of *p*-Nitroaniline. By H. SONNEBORN (*Zeit. Elektrochem.*, 1900, 6, 509).—The electrolytic reduction of *p*-nitroacetanilide in neutral solution, by the method of Elbs (*Zeit. Elek.*

*trochem.*, 1898, 5, 9), with a current density of 0.014 ampère per sq. cm. at the cathode, gave a yield of 30 to 40 per cent. of the theoretical quantity of diacetyl-*p*-diaminoazoxybenzene, and 50 to 60 per cent. of the theoretical quantity of acetyl-*p*-phenylenediamine. It was not found possible to reduce the diacetylazoxy-compound itself further, but *p*-diaminoazoxybenzene was readily reduced electrolytically to the corresponding azo- and hydrazo-compounds. When the solution of *p*-nitroacetanilide is slightly acidified with acetic acid, the reduction yields acetyl-*p*-phenylenediamine, and none of the azoxy-compound.  
T. E.

**Metallic Compounds of Diphenylcarbazone.** By PAUL CAZENEUVE (*Compt. rend.*, 1900, 130, 1478—1479).—Diphenylcarbazone,  $\text{N}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ , obtained by the action of oxidising agents on *s*-diphenylcarbazide, yields metallic derivatives of the type



the *potassium* and *sodium* derivatives are produced either by heating the diphenylcarbazide with alcoholic potash or soda, or by treating it with potassium or sodium in toluene solutions. These alkali derivatives yield the *zinc*, *lead*, *copper*, *mercury*, *iron*, *chromium*, *cobalt*, and *nickel* compounds by double decomposition with the metallic acetates. These substances are soluble in alcohol, benzene, carbon disulphide, or chloroform, but not in water. Platinic chloride gives a *platinum* derivative, but gold chloride and silver salts are reduced by the alkali derivatives of diphenylcarbazone.

These metallic derivatives are all decomposed by heat at temperatures below  $100^\circ$ .  
G. T. M.

**Cuprous and Mercurous Derivatives of Diphenylcarbazone.** By PAUL CAZENEUVE (*Compt. rend.*, 1900, 130, 1561—1563. Compare preceding abstract).—*Cuprous diphenylcarbazone*,



prepared by adding an alcoholic solution of *s*-diphenylcarbazide (1 mol.) to an aqueous solution of copper acetate (2 mols.), forms a deep violet precipitate which decomposes explosively at temperatures below  $100^\circ$ ; it is soluble in the ordinary organic solvents. The cuprous compound slowly decomposes when exposed to moist air, and when dissolved in chloroform containing a little alcohol it is rapidly destroyed, yielding *carbodiazoide*,  $\text{CO}(\text{N}:\text{NPh})_2$ , and cuprous chloride.

The production of the cuprous derivative from diphenylcarbazide affords a means of detecting minute traces of copper, the reaction being even more sensitive than that obtained with ferrocyanide; since the product is decomposed by mineral acids, it is, however, necessary to operate in neutral solutions.

*Mercurous diphenylcarbazone*, obtained from aqueous solutions of mercuric acetate as a deep blue precipitate, resembles its cuprous analogue, but is far more stable, and may also be prepared by heating diphenylcarbazide and mercury at  $170$ — $200^\circ$ .

The production of this compound constitutes a delicate test for mercury in combination with nitric and the organic acids; the mercuric haloids and cyanide, however, do not give this reaction.

G. T. M.

**Preparation of a Pure Albumin from White of Egg.** By F. GOWLAND HOPKINS (*J. Physiol.*, 1900, 25, 306—330).—In crystallised egg-albumin there are undoubtedly several proteids; this is shown by the varying rotation and percentage of sulphur in different fractions. Much the same is true for serum-albumin, but the principal experiments here recorded relate to egg-albumin. A modification of the methods previously described led to the preparation of one of these egg-albumins in a crystalline form, which, after repeated fractional crystallisation, shows absolute constancy of rotation ( $-30.7^\circ$ ) and a constant proportion of sulphur (1.57 per cent.); it is practically ash free. The yield is 50 grams and upwards per litre of egg-white. The crystals obtained by the use of ammonium sulphate may be washed free from that salt by a saturated solution of sodium chloride containing 1 per cent. of acetic acid; the crystals retain their form and solubility in water, and ammonium sulphate does not enter into their composition. Comparatively little importance is attached to the kind of acid used in the preparation of the crystals. W. D. H.

**Formation of Bases from Albumin.** By RUDOLF COUN (*Zeit. Physiol. Chem.*, 1900, 29, 283—302).—The compound melting at  $295^\circ$  (Abstr., 1896, 1, 658), obtained by the action of hydrochloric acid on casein, is not, as previously stated, a pyridine derivative, and, on the other hand, is not identical, as was thought at one time, with leucin imide obtained from leucine (from casein), as the latter melts  $33^\circ$  lower. Although the analyses do not agree very well, and the carbon is 0.9 per cent. too high, the author thinks the compound may be isomeric with leucinimide.

Leucinimide, when reduced with sodium and alcohol, yields a base distilling at  $220-270^\circ$ ; the *hydrochloride*,  $C_{12}H_{26}N_2 \cdot 2HCl$ , can be crystallised from concentrated hydrochloric acid; the *nitrate* crystallises in small plates, and is only sparingly soluble in cold water; and the *platinichloride* crystallises in pale yellow plates. The constitution  $NH \langle \begin{smallmatrix} CH(C_4H_9) \cdot CH_2 \\ CH_2 \cdot CH(C_4H_9) \end{smallmatrix} \rangle NH$  is suggested for the base, and  $NH \langle \begin{smallmatrix} CH(C_4H_9) \cdot CO \\ CO \cdot CH(C_4H_9) \end{smallmatrix} \rangle NH$  for leucinimide. The compound melting at  $295^\circ$  appears to yield the same base when reduced. J. J. S.

**Nucleic Acid from Various Sources.** By LÉON HERLANT (*Chem. Centr.*, 1900, i, 870; from *Arch. exp. Path. Pharm.*, 44, 148—159).—Nucleic acid from unripe salmon sperm was isolated by the "copper-potash method," and the formula of the acid is given as  $C_{40}H_{56}N_{11}O_{16}(P_2O_5)_2$ . That from calf's thymus has the same formula. That from yeast yields, on decomposition, guanine, adenine, and a reducing substance. W. D. H.

**Proteids.** By ALBRECHT KOSSEL and FR. KUTSCHER (*Sitzungsber. Ges. gesammte. Naturwissenschaft. Marburg*, 1900, April 6).—Further investigations into the protamines and proteids proper, with special reference to the bases obtainable from them, leads to the following classification. The protamines that contain a monohexon nucleus



(arginine) fall into two groups, those which yield tyrosine, namely, cyclopteryne, and those which do not, namely, salmine, clupeine, and scombrine. No protamine with a dihexon nucleus is known. Sturine is an instance of a protamine which contains a trihexon nucleus, that is, it yields lysine, arginine, and histidine; it is free from tyrosine. Passing to the proteids proper, none with a monohexon nucleus is known; those with a dihexon nucleus are gluten-fibrin, mucedin, gliadin, and spongin; these yield arginine and histidine, except spongin, which yields arginine and lysine. The proteids with a trihexon nucleus are histon (?), casein, fibrin, fibrin-peptone, gluten-casein, gelatin, and elastin.

W. D. H.

**Glutineptone Hydrobromide and Hydriodide.** By CARL PAAL (*Chem. Zeit.*, 1900, 24, 145. Compare Abstr., 1892, 895; 1898, i, 456; and Levites, *Chem. Zeit.*, 1900, 24, 97).—Quantitative yields of these salts have been obtained by methods similar to that employed in the preparation of the hydrochloride. When concentrated aqueous solutions of the salts are supersaturated with ammonium sulphate, the propeptone salts are precipitated, and may be isolated by extraction with absolute methyl alcohol; the true peptone salts remain in solution and may be separated from the ammonium sulphate by precipitating the latter with absolute ethyl alcohol. The *hydrobromide*, like the hydrochloride, is stable, but the *hydriodide* readily turns yellow, and when kept for some time evolves ethyl iodide and yields the free peptone. Neither salt reacts with Millon's reagent.

J. J. S.

**Thymine.** By H. STEUDEL and ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1900, 29, 303—306).—When thymine is treated with phosphorus oxychloride according to Gabriel and Colman's method (Abstr., 1899, i, 638), a product is obtained which is somewhat similar to, and probably isomeric with, their 2:6-dichloro-4-methylpyrimidine. This *dichlorothymine*,  $C_5H_4N_2Cl_2$ , crystallises in plates, melts at 25—26°, is readily soluble in most solvents, and has a characteristic odour.

J. J. S.

**Amount of Iron Present in the Hæmoglobin of the Horse.** By LOUIS LAPICQUE and H. GILARDONI (*Compt. rend.*, 1900, 130, 1333—1335).—Considerable discrepancy exists between the recorded values of the amount of iron present in the hæmoglobin of the horse; Hoppe-Seyler and the earlier investigators gave the percentage as 0.45—0.47, whilst Bunge and also Zinoffski found 0.335. The composition of the hæmoglobin, rapidly extracted from fresh blood by Jacquet's process, is invariable, the analyses of several preparations giving a practically constant amount, namely, 0.29—0.30; the product obtained by the older and slower methods is less uniform, and the percentage of iron varies from 0.29 to 0.34. This variation is probably due either to changes produced by the putrefaction of the blood or to the action of the chemical agents employed by some investigators in removing the stroma.

These results tend to show that in the blood itself there is only one variety of hæmoglobin, and that the differentiation into several modifi-

cations, containing different amounts of iron, takes place during extraction (compare Cazeneuve and Breteau, *Abstr.*, 1899, ii, 440).

G. T. M.

**Hydrolysis of Fibrous Tissue.** By ALEXANDRE ÉTARD (*Compt. rend.*, 1900, 130, 1263—1265).—When the dried ligamentum nuchæ of the ox is boiled with 20 per cent. sulphuric acid for 24 hours, the product neutralised with chalk, and the filtrate concentrated, a crystalloid substance is obtained which has the colour, taste, and consistence of candied honey. The yield of this product is 116·5 per cent., calculated on the weight of fibrous tissue taken, and if the latter substance be assumed to have the simplified formula,  $C_{48}H_{78}N_{13}O_{16}$ , then the hydrolysis takes place in accordance with the following equation :  $C_{48}H_{78}N_{13}O_{16} + 10H_2O = 3NH_3 + C_{48}H_{78}N_{10}O_{26}$ . Leucine could not be detected in the product of hydrolysis ; the latter, on oxidation with chromic acid mixture, yields ammonium sulphate, oxalic and carbonic acids, traces of hydrocyanic acid, but no acids of the acetic series. The substance behaves quite unlike leucine when distilled with lime or zinc dust, the amount of pyridine bases formed being barely 3 per cent.

G. T. M.

**Action of Papain on Pepsin and Pancreatin.** By V. HARLAY (*J. Pharm.*, 1900, [vi], 11, 466—469).—Not only are pancreatin and papain without destructive action on each other, but the digestive action of either one is favoured by the presence of the other. Pepsin is without action on papain, but papain in a neutral or slightly acid medium partially destroys pepsin.

H. R. LE S.

**Tyrosinase.** By C. GESSARD (*Compt. rend.*, 1900, 130, 1327—1330).—A decoction of tyrosinase in glycerol, obtained from mushrooms by Bourquelot's method, oxidises tyrosine, developing a red coloration, which subsequently turns black ; after some time, an amorphous, black precipitate is formed. If a very small quantity of the diastase is employed, the red coloration persists and the precipitate is not produced. This result indicates that the development of the black coloration and the formation of the precipitate is not due to the tyrosinase, but to some other substance which accompanies it in the glycerol extract. The addition of various metallic salts to solutions of tyrosine containing only traces of tyrosinase promotes the formation of the black precipitate, the action being accelerated by heat. Ammonium phosphate and the salts of magnesium and the alkaline earth metals are especially efficacious in promoting this oxidation. The black substance possesses noteworthy adhesive properties, and is completely precipitated on shaking the solution with some finely-divided, insoluble substance such as talc, starch, calcium carbonate, or magnesium phosphate. When a piece of silk is immersed in the red tyrosine solution, the black precipitate is produced on the fibre, and is not removed by treating the fabric with hot water.

G. T. M.

## Organic Chemistry.

**Quaternary Paraffins. II.** By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1900, **33**, 1905—1908. Compare *Abstr.*, 1899, i, 554).—*ββ-Dimethylpentane* (*trimethylpropylmethane*), prepared by the action of a slight excess of zinc propyl or zinc iodopropyl on *tert*-butyl iodide, boils at 78° under 743 mm. pressure, and has a sp. gr. 0.6910 at 0°/0°, and 0.6743 at 20°/0°; it is not acted on by concentrated nitric acid, or by dilute nitric acid of sp. gr. 1.125—1.40 after heating for 9 hours at 100°, although on heating the hydrocarbon with acid of sp. gr. 1.235 for 27 hours at 110—115°, the secondary *nitro*-derivative,  $\text{CMe}_3\cdot\text{CHEt}\cdot\text{NO}_2$ , is obtained. This boils at 89—90° under 40 mm. pressure, is decomposed on distilling under atmospheric pressure, and has a sp. gr. 0.9520 at 0°/0°, and 0.9401 at 20°/20°; its structure follows from its yielding ethyl *tert*-butyl ketone (boiling at 125.5—126°, and of sp. gr. 0.8258 at 0°/0°, 0.8106 at 20°/0°; compare Wischnegradsky, *Abstr.*, 1875, 878), when its solution in aqueous sodium hydroxide is added to stannous chloride dissolved in hydrochloric acid. That only one *nitro*-derivative is formed during the nitration of the hydrocarbon is shown by the fact that only one *semicarbazone* (melting at 173—174° on rapidly heating) could be isolated from the foregoing ketonic product. The *amine*,  $\text{CMe}_3\cdot\text{CHEt}\cdot\text{NH}_2$ , obtained by reducing the *nitro*-derivative, yields an *aurichloride* crystallising in small needles.

*ββ*-Dimethylpentane was isolated from a fraction of Caucasian naphtha boiling at 78—80° by freezing out the hexanaphthene by means of liquid air, removing tertiary hydrocarbons by fuming sulphuric acid, and finally purifying the oil by digesting successively with nitric acid of sp. gr. 1.15 at 110—115°, and boiling nitric acid of sp. gr. 1.4; the hydrocarbon thus obtained boiled at 78.5—79° under 757 mm. pressure, and had a sp. gr. 0.7083 at 0°/0°, and 0.6921 at 20°/0°.

W. A. D.

**Hydrogenation of Ethylene in the Presence of Reduced Metals.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, **130**, 1761—1764. Compare *Abstr.*, 1897, i, 305, 545).—When a mixture of ethylene and hydrogen is passed over recently reduced cobalt, there is at first a production of ethane accompanied by a rise of temperature; the reaction is, however, not maintained, and as soon as the cobalt becomes slightly carburised, it ceases altogether. At 100—150°, the reaction becomes permanent, and the issuing gas consists of a mixture of ethane, ethylene, and hydrogen, containing traces of higher hydrocarbons of the acetylene series. A certain amount of carbon combines with the cobalt, and as a result the activity of the metal gradually diminishes. At 300°, a small quantity of liquid hydrocarbons is produced, and the gaseous product contains both methane and ethane together with a considerable amount of uncombined ethylene and hydrogen.

Reduced iron has no action on the mixed gases at the ordinary temperature, and even above  $180^{\circ}$  the action is very slow and decreases as the metal becomes carburised.

The combination of ethylene and hydrogen is not induced by reduced copper at temperatures below  $180^{\circ}$ . Between  $180^{\circ}$  and  $300^{\circ}$ , ethane is practically the sole product of combination, there being no appreciable secondary reaction and no deposition of carbon.

G. T. M.

**Action of Acetylene on Cuprous Chloride dissolved in Potassium Chloride Solution.** By R. CHAVASTELON (*Compt. rend.*, 1900, 130, 1634—1636).—The purple compound formed when acetylene is passed through potassium chloride solution containing cuprous chloride is identical with the compound  $C_2H_2 \cdot Cu_2Cl_2 \cdot Cu_2O$ , obtained by the action of water on the compound  $C_2H_2 \cdot Cu_2Cl_2$ , and its formation is limited by the presence of hydrochloric acid in quantity which must be greater the lower the temperature. If the solution of potassium chloride, saturated with cuprous chloride, contains not less than 4 c.c. of concentrated hydrochloric acid in 100 c.c., the first product of the action of acetylene is a yellow, crystalline compound, whilst the final product forms colourless crystals. The first can be converted into the second by the prolonged action of acetylene, and, on the other hand, the white compound is converted into the yellow by the action of a current of carbon dioxide which slowly removes part of the acetylene.

C. H. B.

**Crystalline Compounds of Acetylene with Cuprous and Potassium Chlorides.** By R. CHAVASTELON (*Compt. rend.*, 1900, 130, 1764—1766. Compare preceding abstract).—The colourless crystals which have the composition  $C_2H_2(Cu_2Cl_2)_2 \cdot KCl$ , lose one-half of the combined acetylene and become converted into the yellow compound  $C_2H_2[(Cu_2Cl_2)_2 \cdot KCl]_2$  by washing with ether or with the original solution of cuprous and potassium chlorides. Both these double salts have very low dissociation pressures at the ordinary temperature, and they can therefore be dried in a current of carbon dioxide without decomposition. They dissolve in dilute hydrochloric acid without dissociation, the yellow compound being the more soluble. When treated with water, both compounds yield the substance  $C_2H_2 \cdot Cu_2Cl_2 \cdot Cu_2O$ , whilst cuprous acetylide results from the action of ammonia.

G. T. M.

**Mode of Formation of the Compounds  $C_2H_2(Cu_2Cl_2)_2 \cdot KCl$  and  $C_2H_2[(Cu_2Cl_2)_2 \cdot KCl]_2$ .** By R. CHAVASTELON (*Compt. rend.*, 1900, 131, 48—50. Compare preceding abstracts).—In solutions saturated with the yellow compound, the ratio of combined to total cuprous chloride is 0.25, whilst in solutions saturated with the colourless salt this quotient is 0.20.

G. T. M.

**Hydrogenation of Acetylene in Presence of Reduced Iron or Cobalt.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 130, 1628—1630).—When acetylene mixed with an excess of hydrogen is passed over reduced iron, there is no change at

the ordinary temperature, but above  $180^{\circ}$  condensation takes place with production of ethane, ethylene, and higher hydrocarbons of the ethylene series boiling between  $50^{\circ}$  and  $250^{\circ}$ , together with small quantities of benzene and its homologues.

With reduced cobalt above  $180^{\circ}$ , the acetylene is almost completely converted into ethane, together with some liquid paraffins, the proportion of the latter increasing with the temperature.

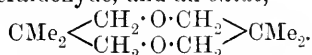
It is clear therefore that different metals produce very different results with mixtures of acetylene and hydrogen. In all cases, if the acetylene is in excess, it is decomposed with liberation of carbon in the manner observed by Moissan and Moureu. C. H. B.

**Hydrogenation of Acetylene and Ethylene in the Presence of Finely-divided Platinum.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 131, 40—42. Compare Abstr., 1899, i, 555).—When a mixture of acetylene and hydrogen containing an excess of the latter is passed over platinum black at the ordinary temperature, the hydrocarbon is completely hydrogenised to ethane; if, however, the acetylene is in excess, both ethylene and ethane are produced. At  $180^{\circ}$ , the formation of these gaseous products is accompanied by condensations giving rise to liquid hydrocarbons. The catalytic action of platinum black on mixtures of ethylene and hydrogen is only temporary at the ordinary temperature; at  $100$ — $120^{\circ}$ , there is a slow combination, whilst at  $185^{\circ}$  the reaction is practically quantitative.

Spongy platinum does not induce the hydrogenation of acetylene or ethylene at the ordinary temperature; at  $180^{\circ}$ , however, it behaves like platinum black. G. T. M.

**Action of Reduced Nickel on Acetylene.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 131, 187—190. Compare Abstr., 1899, i, 553; this vol., i, 197, and preceding abstracts).—A rapid current of acetylene, passed over nickel reduced by hydrogen and cooled in a current of this gas, at once produces incandescence; this reaction is due to the presence of hydrogen, for when it is displaced by nitrogen, there is no appreciable action at temperatures below  $180^{\circ}$ . At higher temperatures, a slow reaction sets in, and is maintained without incandescence, provided that the current of acetylene is not too rapid; the issuing gas contains hydrogen, ethane, ethylene, together with unchanged acetylene, liquid hydrocarbons containing benzene and the higher olefines are simultaneously produced, and the solid residue appears to consist of a mixture of metallic carbide with a solid hydrocarbon, the latter being analogous to the euprone obtained from copper and acetylene. When a rapid current of acetylene is employed, the condensation is attended by incandescence, and the issuing gas consists of 51.4 per cent. of hydrogen, 36.3 per cent. of ethane, 2 per cent. of ethylene, 10.3 per cent. of benzene and its homologues, and traces of acetylene; the liquid product is a mixture of aromatic and unsaturated hydrocarbons boiling between  $50^{\circ}$  and  $180^{\circ}$ , and the experimental tubes contain a mixture of nickel with carbon and a solid hydrocarbon resembling euprene. G. T. M.

**Action of Sulphuric Acid on Dimethylpropanediol.** By ALOIS FISCHER and BERTHOLD WINTER (*Monatsh.*, 1900, 21, 301—318).—Pentaglycol (Abstr., 1894, i, 353), when heated with 20 per cent. sulphuric acid in a sealed tube at 200° for 3 hours, yields methyl *iso*-propyl ketone, *isovaleraldehyde*, and an *oxide*,



The last is a colourless, refracting liquid which boils at 180°, yields, when oxidised with alkaline permanganate, dimethylmalonic acid, and, when treated with hydrogen bromide, a mixture of trimethylene dibromide and pentaglycol dibromide. R. H. P.

**A Product of the Decomposition of Glycerol Diiodohydrin.** By ERNEST CHARON and C. PAIX SÉAILLES (*Compt. rend.*, 1900, 130, 1631—1633).—The compound of the empirical composition  $\text{C}_3\text{H}_5\text{OI}$ , formed by the removal of the elements of hydrogen iodide from glycerol diiodohydrin is *para*- $\beta$ -iodopropaldehyde; it forms slender, white needles which melt at 160°, sublime very easily, and are very stable when exposed to light, and is best obtained by heating the glycerol diiodohydrin at 100° under reduced pressure, some allyl iodide and polyiodopropanes being also formed. The results obtained by heating the diiodohydrin with alkalis, lead hydroxide, or silver oxide, are less satisfactory. When heated with solid potassium hydroxide, *para*- $\beta$ -iodopropaldehyde yields metacraldehyde. C. H. B.

**Partial Synthesis of *l*-Erythritol.** By LÉON MAQUENNE (*Bull. Soc. Chim.*, 1900, [iii], 23, 587—591).—The synthesis of *l*-erythritol has been effected by applying to xylose the process of degradation by which Wohl (this vol., i, 140) has obtained *l*-erythrose from *l*-arabinose. A number of new compounds have thus been obtained. *Xylosoxime*, obtained by the action of hydroxylamine on xylose in alcoholic solution, forms an uncrystallisable, viscous mass which becomes semi-fluid at 100°, and is very soluble in water or alcohol. When heated with acetic anhydride and sodium acetate, it is converted into *acetylxylosonic nitrile*, which crystallises in white or pale yellow scales melting at 81.5°, and is decomposed by alkalis with the production of a considerable quantity of erythrose. By treatment with ammonia (the addition of silver oxide, recommended by Wohl, is considered rather to retard the reaction), the nitrile is converted into *erythrose-acetamide*, which crystallises in small, colourless prisms melting at 166°, and is hydrolysed by mineral acids with the formation of *l*-erythrose, whence *l*-erythritol is obtained by reduction with sodium amalgam. *l*-Erythritol, which was separated by means of its benzaldehyde derivative, crystallises from alcohol in slender needles, and from water in elongated prisms melting sharply at 88°; it is very soluble in water, and is more soluble in hot alcohol than its inactive isomeride. Its rotatory power in 6 per cent. aqueous solution is  $[\alpha]_D + 4.3^\circ$ , whilst in 1.5 per cent. alcoholic solution it is  $[\alpha]_D - 15^\circ$ . N. L.

**Methyl Ester and Amide of *d*-Valeric Acid (Methyl-2-butan-*oic* acid) and the Solubility of its Silver Salt.** By H. J. TAVERNE (*Rec. Trav. Chim.*, 1900, 19, 107—110).—*Methyl d*-valerate

obtained, by saturating a mixture of its generators with hydrogen chloride, is a liquid having an agreeable odour; it boils at 115° under 760 mm. pressure, has a sp. gr. 0.8931 at 15°, and has  $[\alpha]_D + 16.13'$ . The *amide*, prepared by treating the ester with ammonia, crystallises from light petroleum in leaflets melting at 111°; it has  $[\alpha]_D + 18.19'$ . The solubility of silver *d*-valerate in water is 0.680—0.732 part per 100, and not 1.16 as previously stated. G. T. M.

**Telfairia Oil.** By HERMANN THOMS (*Arch. Pharm.*, 1900, 238, 48—58).—This oil is contained in the seeds of *Telfairia pedata*, Hook, a gourd-like, climbing plant which grows in East Africa. In a sample from Kwais in Usambara, the kernel formed 60 per cent. of the seed, and contained 64.7 per cent. of oil. The oil had the following constants: sp. gr., 0.9180 at 15°; acid number, 0.34; saponification number, 174.8; ester number, 174.5; acetyl number, 26.9; iodine number, 86.2; freezing point of the oil, 7°; melting point of the fatty acids, 44°; freezing point of the same, 41°; refractometer number, 61—62 at 31° to 63—64 at 25°. The oil is to a slight extent a drying oil, and it gives an unpleasant odour when heated; for these reasons, and on account of its comparatively high freezing point, it can hardly replace olive oil for culinary purposes. In its hydrolysis, glycerol is formed; the lead salts of the fatty acids were separated by extraction with ether into a solid portion, which contained palmitic and stearic acids, but no hydroxy-acid, and a liquid portion. The latter yielded acids which were separated by distillation under diminished pressure into a new acid, telfairic acid, and a fraction of higher boiling point, approximately having the composition  $C_{24}H_{40}O_3$ . *Telfairic acid*,  $C_{15}H_{32}O_2$ , is isomeric with linoleic acid, &c.; it boils at 220—225° under 13 mm. pressure, and freezes at 5—2°; it forms a *tetrabromide*,  $C_{15}H_{32}O_2Br_4$ , which melts at 57—58°; like linoleic acid, it yields tetrahydroxystearic (sativic) acid when oxidised with dilute permanganate at 0°, and azelaic (leparglylic) acid when the oxidation is effected at the ordinary temperature. C. F. B.

**Anhydrous Acrylic Acid.** By EINAR BJELLMANN [in part with BJERRUM] (*J. pr. Chem.*, 1900, [ii], 61, 491—494).—Anhydrous acrylic acid can be prepared by the action of reduced copper containing a trace of iron on  $\alpha\beta$ -dibromopropionic acid. The pure anhydrous acid melts at 10.1—10.2°, and boils at 140.8—141°; by vigorous boiling, the anhydrous acid polymerises to some extent to a white compound, which was not further investigated. T. M. L.

**Glyoxylic Acid.** By OSCAR DOEBNER (*Annalen*, 1900, 311, 129—131).—Existing methods for preparing glyoxylic acid are unsatisfactory, but the following process is found to be trustworthy. Dichloroacetic acid (65 parts) is neutralised exactly with potassium hydroxide (1:1) and heated with solid potassium acetate (100 parts) in a reflux apparatus during 1 hour; the filtered liquid, which contains potassium diacetoxyacetate, is boiled with 10 volumes of water in a reflux apparatus during several hours, yielding potassium glyoxylate and free acetic acid. M. O. F.

**Ethyloxalic Anhydride.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 509—511).—When ethyloxalic chloride (ethyl chloroglyoxylate) is heated with a mol. proportion of sodium acetate and the product of the reaction fractionally distilled under diminished pressure, the mixed acetic ethyloxalic anhydride first formed is decomposed into the two simple anhydrides. *Ethyloxalic anhydride*,  $(\text{CO}_2\text{Et}\cdot\text{CO})_2\text{O}$ , is a colourless, oily, very hygroscopic liquid which boils at  $135^\circ$  under 100 mm. pressure. The experiments of Rousset (*Abstr.*, 1895, i, 592) and Béhal (this vol., i, 8) on mixed anhydrides are referred to in connection with the method employed for the preparation of this compound. N. L.

**Synthesis of Higher Homologues of Ethyl Acetoacetate and Acetylacetone.** By LOUIS BOUVEAULT (*Compt. rend.*, 1900, 131, 45—48).—*Ethyl isobutyrylacetoacetate*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , produced together with its *isomeride*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , by the action of *isobutyric* chloride on the sodium derivative of ethyl acetoacetate, is separated from the latter by dissolving in barium hydroxide solution and reprecipitating with acid; it is a colourless liquid boiling at  $114^\circ$  under 15 mm. pressure; the other compound, which is insoluble in alkaline solutions, is a colourless liquid having a characteristic odour and boiling at  $117^\circ$  under 15 mm. pressure. When hydrolysed with hydrochloric acid and water at  $140$ — $150^\circ$ , the *isobutyrylacetoacetate* is decomposed into methylisopropylacetone, ethyl alcohol, and acetic and carbonic acids.

*isoButyrylacetone*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{Ac}$ , is formed when water only is employed in the preceding hydrolysis; it is a colourless liquid which has an agreeable odour and boils at  $168^\circ$ . It yields a volatile copper salt which dissolves in a mixture of chloroform and petroleum and separates in blue crystals which become pink on exposure to the air.

*Ethyl isobutyrylacetate*, obtained by hydrolysing ethyl *isobutyrylacetoacetate* with 1 mol. of sodium hydroxide dissolved in water or alcohol, is a colourless liquid having a fruity odour; it boils at  $93$ — $94^\circ$  under 16 mm. pressure. This substance is readily decomposed by alkalis, yielding methylisopropylacetone, ethyl alcohol, and carbon dioxide. G. T. M.

**$\alpha\beta$ -Dimethylglutolactonic Acid.** By EDMOND E. BLAISE (*Compt. rend.*, 1900, 130, 1716—1719. Compare *Abstr.*, 1896, i, 667).—The semicarbazone of  $\beta$ -methylglutavulic acid (m. p.  $197^\circ$ ) is produced with some difficulty, and when the reaction is prolonged it decomposes into the acid  $\text{N}_2(\text{CMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ ; this substance, when condensed with hydrogen cyanide, yields a liquid which boils at  $144$ — $158^\circ$  under 25 mm. pressure, and contains the nitriles of the isomeric lactonic acids having the general formula  $\text{CH}_2\langle\begin{smallmatrix} \text{CHMe} \\ \text{CO}-\text{O} \end{smallmatrix}\rangle\text{CMe}\cdot\text{CN}$ .

*trans- $\alpha\beta$ -Dimethylglutolactonic acid*,  $\text{CH}_2\langle\begin{smallmatrix} \text{CHMe} \\ \text{CO}-\text{O} \end{smallmatrix}\rangle\text{CMe}\cdot\text{CO}_2\text{H}$ , separates from the product obtained by hydrolysing the mixed nitriles with concentrated hydrochloric acid, in crystals melting at  $142^\circ$ ; it readily dissolves in water, but is somewhat insoluble in cold benzene. The *lead* salt crystallises in white needles and melts at  $212$ — $214^\circ$ .



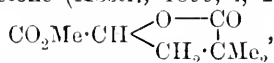
The *cis-isomeride* is separated from the mother liquors in the form of its *lead* salt, this derivative differing from the corresponding *trans*-compound in crystallising with  $11\text{H}_2\text{O}$ ; the hydrated salt melts at  $140\text{--}145^\circ$ , whilst the anhydrous substance melts at  $181\text{--}183^\circ$ . The *acid*, obtained from the lead salt by means of hydrogen sulphide, is a colourless liquid boiling at  $193\text{--}195^\circ$  under 15 mm. pressure; when heated with quinoline and water at  $180^\circ$  for 6 hours, it is converted into the *trans*-modification. G. T. M.

**Oxidation of Cyclic Compounds:  $\alpha$ -Methyladipic Acid.** By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1900, 33, 1908—1910).— $\beta$ -Methylcyclohexanone, on oxidation with nitric acid, gives almost a theoretical yield of what is apparently  $\alpha$ -methyladipic acid,  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ , melting at  $52\text{--}53^\circ$ ; the *ethyl* salt is laevorotatory, and boils at  $160^\circ$  under 40 mm. pressure, and at  $252\text{--}253^\circ$  with partial decomposition under the ordinary pressure. The acid is probably identical with that obtained on oxidising  $\beta$ -methylcyclohexanone with aqueous potassium permanganate, which Wallach first considered to be  $\alpha$ -methyladipic acid (*Annalen*, 1896, 289, 345), but later (*Ber.*, 1899, 32, 3339) concluded was the  $\beta$ -acid.

The oxidation of pulegone with nitric acid is less simple, a considerable quantity of oxalic acid being formed.  $\beta$ -Methyladipic acid is obtained on oxidising pulegone with aqueous potassium permanganate, as stated by Semmler, and from menthone by a similar process (Manasse and Rupe); but in each case the yield is only 50 per cent. of the theoretical, pyrotartaric acid and other substances being formed.

W. A. D.

**Synthesis of  $\alpha\alpha$ -Dimethylglutaconic Acid.** By MAX CONRAD (*Ber.*, 1900, 33, 1920—1922).—The *methyl* ester of  $\gamma$ -hydroxy- $\alpha\alpha$ -dimethylglutaric acid lactone (*Abstr.*, 1899, i, 259),



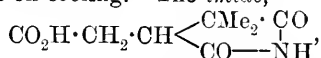
obtained by passing hydrogen chloride into a methyl alcoholic solution of the lactone, crystallises in long, colourless prisms melting at  $68^\circ$ , and when boiled with a solution of sodium in amyl alcohol, then poured into water and again boiled, is converted into  $\alpha\alpha$ -dimethylglutaconic acid,  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ . This is best purified by conversion into its insoluble barium salt, and after repeated crystallisation melts sharply at  $150^\circ$ . It is probably identical with the acid described by Henrich (*Abstr.*, 1899, i, 469, 794), although he gives the melting point as  $126\text{--}133^\circ$ .

J. J. S.

**Synthesis of Ethyl  $\beta$ -Cyano- $\alpha\alpha$ -dimethyltricarballoylate and  $\alpha\alpha$ -Dimethyltricarballoylic Acid.** By ALBIN HALLER and G. BLANC (*Compt. rend.*, 1900, 131, 19—22).—Ethyl  $\beta$ -cyano- $\alpha\alpha$ -dimethyltricarballoylate,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{CN})(\text{CO}_2\text{Et})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , produced by heating together in absolute alcohol molecular proportions of ethyl cyanosuccinate, sodium ethoxide, and ethyl  $\alpha$ -bromo*isobutyrate*, is a colourless liquid with an alliaceous odour and boils at  $205\text{--}206^\circ$  under 21 mm. pressure.

$\alpha\alpha$ -Dimethyltricarballoylic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,

obtained by hydrolysing the preceding ester with 10 per cent. hydrochloric acid, separates in small crystals melting at  $155^{\circ}$ ; when treated with a boiling solution of copper acetate, it yields a light blue precipitate which redissolves on cooling. The *imide*,



simultaneously produced during this hydrolysis, crystallises from water in colourless prisms and melts at  $182-183^{\circ}$ ; it is a monobasic acid, readily hydrolysed by potassium hydroxide into the corresponding tricarballic acid. G. T. M.

**Interaction of Ammonium Cyanide with Acetone.** By WLADIMIR VON GULEWITSCH (*Ber.*, 1900, 33, 1900—1901).—When acetone is left at the ordinary temperature with a freshly prepared 3 per cent. solution of ammonium cyanide (1 mol.) for 19 hours, and the solution subsequently boiled for 4 hours with dilute hydrochloric acid, 74 per cent. of the theoretical quantity of  $\alpha$ -aminobutyric acid is obtained; when the mixture is left only  $\frac{1}{2}$  hour at the ordinary temperature, the yield is very much diminished, although, according to Ljubawin (*Abstr.*, 1883, 178), these conditions are the most favourable in the case of the interaction of ammonium cyanide with aldehydes.

W. A. D.

**Degradation of *d*-Galactose and of Lactose: *d*-Lyxose and Galactoarabinose.** By OTTO RUFF and GERHARD OLLENDORFF (*Ber.*, 1900, 33, 1798—1810).—*d*-Lyxose (Fischer and Bromberg, *Abstr.*, 1896, i, 348; Wohl and List, *Abstr.*, 1898, i, 168) is readily prepared by oxidising calcium galactonate with hydrogen peroxide in presence of basic ferric acetate (compare Ruff, *Abstr.*, 1898, i, 516; 1899, i, 324, 869; 1900, i, 139); it forms colourless, transparent, hygroscopic, monoclinic crystals [ $a:b:c = 1.6076:1:1.8277$ ,  $\beta = 117^{\circ}50'$ ], sinters at  $99^{\circ}$ , melts at  $101^{\circ}$  (corr.), and shows mutarotation; an aqueous (?) solution, which 4 minutes after preparation had  $[\alpha]_D - 3^{\circ}$ , had  $[\alpha]_D - 13.9^{\circ}$  after 24 hours. One part of *d*-lyxose dissolves in 37.97 parts of absolute alcohol, and 1 mg. reduces 1.793 mg. of copper according to Allihn's method. The sugar is not fermentable. *d*-Lyxosephenylbenzylhydrazone crystallises from 30 per cent. alcohol in slender, white needles, with  $\text{H}_2\text{O}$ , which melt at  $116^{\circ}$ ; from absolute alcohol, the anhydrous substance is obtained in hard prisms melting at  $128^{\circ}$ , whilst in the same solvent  $[\alpha]_D + 26.39^{\circ}$ . On reducing *d*-lyxose with sodium amalgam, *d*-arabitol (Ruff, *Abstr.*, 1899, i, 324) is obtained. The foregoing facts are in complete accord with Fischer's views as to the configuration of *d*-galactose, *d*-lyxose, and *d*-arabitol.

Lactobionic acid, on oxidation with hydrogen peroxide and ferric acetate, is transformed into a disaccharide, with 11 carbon atoms, to which the name *galactoarabinose* is given, since on hydrolysis with dilute sulphuric acid it yields *d*-arabinose and *d*-galactose; it forms a colourless, cupric-reducing, dextrorotatory syrup which could not be crystallised. The *osazone*,  $\text{C}_{23}\text{H}_{36}\text{O}_8\text{N}_4$ , crystallises from absolute alcohol, and melts when rapidly heated at  $236-238^{\circ}$ . The diphenylhydrazone could not be prepared, but the *phenylbenzylhydrazone*,  $\text{C}_{24}\text{H}_{32}\text{O}_9\text{N}_2$ , crystallises from 50 per cent. alcohol, and has  $[\alpha]_D - 23.7^{\circ}$

in this solvent; it melts at  $223^{\circ}$  (corr.), and when treated with aqueous formaldehyde regenerates the disaccharide. The production of galactoarabinose from lactose by the foregoing method through lactobionic acid supports Fischer's contention (Abstr., 1888, 1267; 1889, 485) that the aldehyde group of lactose is present in the glucose portion of the molecule, and is not in agreement with the opposite conclusion recently arrived at by de Bruyn and Alberda van Ekenstein (Abstr., 1899, i, 661).

Galactosidogluconic acid, the synthetical product obtained from galactose and gluconic acid (Fischer and Beensch, Abstr., 1894, i, 565), is evidently not identical with lactobionic acid, since it fails to interact with hydrogen peroxide under the conditions already indicated; when action occurs on heating at  $60-70^{\circ}$ , galactoarabinose is not formed, but only *d*-galactose and *d*-arabinose along with glyoxal. The *dibenzylphenylhydrazone* of the latter,  $C_{25}H_{26}N_4$ , forms yellow needles and melts at  $197.5^{\circ}$ .  
W. A. D.

**Specific Heat of Wheat Starch as a Function of Hydration and Temperature.** By HERMANN RODEWALD and A. KATTEIN (*Zeit. physikal. Chem.*, 1900, 33, 540—544).—The specific heats of wheat starch, containing from 0 to 33.6 per cent. of water, were determined at different temperatures. The temperature coefficients vary from 0.0006 to 0.0012, and the values at zero vary from 0.2697 to 0.3054, but not uniformly, as they first decrease, then increase, and again decrease with increasing hydration.  
L. M. J.

**Natural and Artificial Starch Grains.** By HERMANN RODEWALD and A. KATTEIN (*Zeit. physikal. Chem.*, 1900, 33, 579—592).—If starch is brought into solution by heating with iodine at  $130^{\circ}$ , the iodine removed, and the starch precipitated from the solution, the resulting 'artificial' starch closely resembles pure starch grains in all its properties. By the method previously described by Rodewald (Abstr., 1898, ii, 61), the heat produced by soaking in water was determined for various varieties of starch, and a 'soluble amylose' at various degrees of hydrations. Curves and formulae reproducing them are given, the differences between the various varieties being but slight. Osmotic measurements were made with starch iodide solution, membranes of parchment and of collodion being employed; these indicated values of 39,680 and 36,740 for the mol. weight of the starch. The artificial starch has a density 1.661, that of the wheat starch from which it was prepared being 1.6427. It dissolves in alkali, the solution being strongly dextrorotatory, the rotation being increased by addition of water, but decreased by more alkali, and in this respect it resembles the soluble amylose, the molecular rotation of the latter being, however, about 8 per cent. higher.  
L. M. J.

**"Swelling" (Quellung) and Wetting.** By HERMANN RODEWALD (*Zeit. physikal. Chem.*, 1900, 33, 593—604).—On the assumption that the heat produced by the wetting or swelling of starch is due to an adhesive force between the starch and water, and is hence proportional to the surface, the author deduces an expression,  $c(w_1 - w_0) = \log(r_0 + i)$

$-\log(r_1 + i)$  for the heat of swelling, where  $w_1$  is the water content and  $r_1$  the heat produced. The experimental data (preceding abstract) were in good accord with the values so calculated. The formula indicates that at a certain water concentration further addition should produce no heat effect, but it was found for all the varieties of starch examined that there was still a heat production of about 0.5 Cal. This is probably due to the supposition that the work of adhesion is proportional to the surface being inexact, as a second layer of water molecules is not in direct contact with starch. The surface area of the water molecules required per milligram of starch was estimated, and hence, assuming that each molecule of starch is surrounded by water molecules, the author calculates the molecular weight of the starch on the assumption (1) of cubic and (2) of spherical molecules, the numbers so obtained varying for the different varieties of starch from 103,300 to 17,430. L. M. J.

Galactosamine, a New Amino-sugar, as a Decomposition Product of the Gluco-proteid of the Albuminous Gland of the Frog. By FRIEDRICH N. SCHULZ and FRITZ DITTHORN (*Zeit. physiol. Chem.*, 1900, 29, 373—385).—This substance, described as a new amino-sugar, was obtained as a decomposition product of the gluco-proteid of the albuminous gland of the frog. The investigation is to be continued with other varieties of so-called mucin. W. D. H.

Halogen Derivatives of Hexamethylenetetramine. By M. HOEHNEL (*Arch. Pharm.*, 1900, 238, 163).—The author regrets having overlooked, in his recent papers (this vol., i, 279) a communication by Horton (Abstr., 1888, 1051) on the same subject. W. A. D.

The Thiocyanoacetic Acids. By GUSTAV FRERICHS and HEINRICH BECKURTS (*Arch. Pharm.*, 1900, 238, 9—15. Compare Claesson, Abstr., 1878, 37; Frerichs, Abstr., 1899, i, 796).—The salts, &c., obtained by Claesson from potassium thiocyanate and salts, &c., of chloroacetic acid are not all derivatives of thiocyanoacetic acid. The amide is derived from this acid,  $\text{CN}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ; the metallic salts and esters, however, from thiocarbimidoacetic acid,  $\text{CS}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , whilst the free acid is a mixture of the two isomeric compounds. The thiocarbimido-derivatives are recognised as such by the fact that they yield hydrogen sulphide and hydrogen cyanide, but no thioglycollic acid, when boiled with alkalis; whereas the thiocyano-compounds yield thioglycollic acid, which is detected by acidifying with hydrochloric acid, adding a trace of ferric chloride and shaking with excess of ammonia, when a violet coloration is formed.

*Thiocarbimidoacetamide*,  $\text{CS}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , obtained by boiling potassium thiocyanate with chloroacetamide in alcoholic solution, melts at  $115^\circ$ ; cold aqueous ammonia transforms it into thiocyanoacetamide.

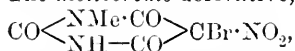
In a later communication (*ibid.*, 317—320), the authors state that they are in error as to the compound melting at  $115^\circ$ ; it had already been described by Miolati (Abstr., 1893, i, 405), who correctly regarded it as thiocyanoacetamide, whilst the product formed from it is thiohydantoin. Similarly, the compounds described by Frerichs (*loc. cit.*)

as thiocynoaceto-derivatives, are in reality the corresponding derivatives of thiohydantoin.  
C. F. B.

**Cyanoselenium Compounds.** By WILHELM MUTHMANN and E. SCHRÖDER (*Ber.*, 1900, 33, 1765—1769).—Potassium selenocyanide is best prepared by fusing pure potassium cyanide with selenium. Cyanogen triselenide is most advantageously obtained by the action of nitric oxide on a paste of potassium selenocyanide with water. Its mol. weight, determined by the boiling point method in benzene and in chloroform solution, corresponds with that required for the accepted formula  $C_2N_3Se_3$ . It acts vigorously on many organic compounds with production of selenium, but the exact course of the reaction has not been ascertained in any one case, as the products appear to be of a complex character.  
A. H.

**Methylvioluric Acid and Methyldilituric Acid.** By RUDOLF ANDREASCH (*Monatsh.*, 1900, 21, 281—300).—*Methylvioluric acid*,  $CO \begin{smallmatrix} \diagup NMe \cdot CO \\ \diagdown NH - CO \end{smallmatrix} > C:N \cdot OH$ , prepared from hydroxylamine hydrochloride and methylalloxan, crystallises, with  $H_2O$ , in slender needles which have a faint yellow tinge; it is moderately acid, decomposing carbonates and acetates, and forms violet-red coloured salts, which decompose when heated, evolving violet fumes; the *potassium, sodium* (with  $1\frac{1}{2} H_2O$ ), *ammonium, calcium, barium, lead* (with  $3H_2O$ ), *cadmium* (with  $6H_2O$ ), *copper* (with  $3H_2O$ ), and *zinc* (with  $H_2O$ ) salts are described.

*Methyldilituric acid*, obtained by the oxidation of methylvioluric acid with nitric acid, crystallises from water in thick prisms which contain  $1\frac{1}{2} H_2O$  and melt at  $143^\circ$ , and is not hydrolysed by alkalis. The *potassium, sodium* (with  $H_2O$ ), *ammonium, barium* (with  $H_2O$ ), *strontium* (with  $3H_2O$ ), *lead* (with  $2\frac{1}{2} H_2O$ ), and *cadmium* (with  $2H_2O$ ) salts are described. The *monobromo-derivative*,



which crystallises in white, microscopic prisms melting at  $138-139^\circ$ , and *monochloro-derivative*, which crystallises in plates melting at  $121^\circ$ , were prepared.  
R. H. P.

**Mercury Antimonide and Stibonium Compounds.** By ALFRED PARTHEIL and E. MANNHEIM (*Arch. Pharm.*, 1900, 238, 166—184).—Although mercury antimonide cannot be prepared by passing hydrogen antimonide through solutions of mercuric chloride (compare Pfaff, *Ann. Phys. Chem.*, 1837, [i], 42, 344; Simon, *ibid.*, 566; Rose, *ibid.*, 1844, [i], 51, 423), it is formed quantitatively according to the equation  $2SbH_3 + 3HgCl_2 = Sb_2Hg_3 + 6HCl$ , when the carefully dried gas is passed through a mixture of dry mercuric chloride and sand contained in a rotating cylinder at the ordinary temperature; the action is, however, somewhat slow. The *antimonide*,  $Sb_2Hg_3$ , is a dark-grey, heavy powder, which when pure is somewhat prone to decomposition, although quite stable when mixed with sand; with warm nitric acid, it yields mercuric nitrate and antimony tetroxide, whilst on heating, the mercury sublimes and the antimony burns to form the trioxide. With ethyl iodide at the temperature of boiling aniline, it yields *tetraethylstibonium mercuriodide*,  $SbEt_4I, HgI_2$ , which

separates from alcohol in whitish-yellow crystals and melts at 93—95°. Tetraethylstibonium iodide,  $\text{SbEt}_4\text{I} \cdot \frac{1}{3}\text{H}_2\text{O}$ ,\* is very soluble in water, but crystallises from it in long needles which begin to decompose at 150°. The salt,  $\text{SbEt}_4\text{Cl} \cdot 4\text{HgCl}_2$ , crystallises from water in small, white octahedra, and melts at 141—142°; the aurichloride,  $\text{SbEt}_4\text{Cl} \cdot \text{AuCl}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , forms yellow needles or plates, darkens at 150°, and melts at 178°; the platinichloride,  $(\text{SbEt}_4)_2\text{PtCl}_6$ , decomposes at 141°. The foregoing salts were also prepared from tetraethylstibonium iodide, obtained by Loewig and Schweitzer's method (*Annalen*, 1850, 75, 315, 338; 1856, 97, 322).

*Tetrapropylstibonium mercuriodide*,  $\text{SbPr}_4\text{I} + \text{HgI}_2$ , prepared either by the action of propyl iodide on mercury antimonide at 180°, or from *tetrapropylstibonium iodide*,  $\text{SbPr}_4\text{I}$ , obtained according to Loewig and Schweitzer's method (*loc. cit.*), crystallises from alcohol in lustrous, yellow prisms, and melts at 103·5°. The base,  $\text{SbPr}_4 \cdot \text{OH}$ , forms long needles which are extremely hygroscopic.

*Tetrapropylstibonium mercurichloride*,  $\text{SbPr}_4\text{Cl} \cdot \text{HgCl}_2$ , crystallises from water in long, silky needles, from alcohol in thick prisms, and melts at 120—121°. The aurichloride,  $\text{SbPr}_4\text{Cl} \cdot \text{AuCl}_3$ , crystallises from 80 per cent. alcohol in beautiful, slender, yellow needles, and melts at 98°; the platinichloride,  $(\text{SbPr}_4)_2\text{PtCl}_6$ , crystallises from dilute hydrochloric acid in stout, yellowish-red octahedra, and melts and decomposes at 133°; the picrate,  $\text{C}_{18}\text{H}_{30}\text{O}_7\text{N}_3\text{Sb}$ , crystallises from 20 per cent. alcohol in small, yellow needles, and melts at 67·5°.

W. A. D.

**Ring-system of Benzene.** By HUGO KAUFFMANN (*Ber.*, 1900, 33, 1725—1742).—The nature of the ring-system in benzene derivatives can be ascertained to some extent by the action of Tesla-rays on their vapours. Luminescent substances are regarded as containing a ring prone to assume a quinone-like structure. Benzene and its homologues, diphenylmethane and dibenzyl, show practically no luminescence, whilst triphenylmethane is only slightly luminescent; naphthalene, anthracene, phenanthrene, acenaphthene, and chrysene are luminescent and are readily oxidised to quinones, and diphenyl, carbazole, and diphenylene oxide are also luminescent. The phenols are not luminescent, but catechol and resorcinol are slightly luminescent, and quinol and the trihydric phenols are strongly so, with the exception of pyrogallol, which does not contain a *p*-hydroxyl group and is only slightly luminescent; the phenol ethers are usually more luminescent than the phenols from which they are derived, although they are less readily oxidised to quinones. The amines are all luminescent, and more strongly so when alkylated, when two amino-groups are present or when a hydroxyl group is also present; tetrahydroquinoline and 1-methyltetrahydroquinoline are strongly luminescent, but not quinoline. Acetyl and benzylidene groups usually diminish the luminescence, and nitro-groups destroy it altogether, a result which is in accordance with the additional stability which they impart to the ring; chlorine also decreases it, bromine

\* Loewig and Schweitzer describe tetraethylstibonium iodide with  $1\text{H}_2\text{O}$ .—W. A. D.

acts still more powerfully, whilst carboxylic acids and esters are usually entirely without luminescence.

It is remarkable that the quinones themselves, and all coloured benzene derivatives, are entirely non-luminescent; auxochromes increase the luminescence, chromophores decrease it. The leuco-compounds are, however, luminescent.

In the case of the phenazonium derivatives, the ring which will act as a quinone is that which contains luminescent groups, such as naphthalene in place of benzene or an amino- or hydroxyl group, and these groups increase the readiness with which substitution takes place; on the other hand, nitro-groups, &c., which decrease the luminescence, also protect the ring from attack. T. M. L.

**Nitration of Nitrobenzene.** By ARNOLD F. HOLLEMAN and B. R. DE BRUYN (*Rec. Trav. Chim.*, 1900, 19, 79—110. Compare this vol., i, 387).—A detailed account of a study of the nitration of nitrobenzene, made with a view of ascertaining (1) the relationship existing between the weights of the three isomerides produced; (2) the absolute value of the velocity constants of the reaction.

The relative proportions by weight of the three dinitrobenzenes are determined by a solubility method similar to that employed in the case of the nitrobenzoic acids (*Abstr.*, 1899, i, 282, 757; ii, 257). Dilute ethyl alcohol is employed as the solvent, and it is found that the solubility of any one of the dinitrobenzenes is not appreciably altered by the presence of its isomerides. The solution being saturated with two of the isomerides, the amount of the third present is indicated by the sp. gr. of the liquid, and tables and curves may be constructed by which the quantity of dissolved *o*- or *p*-dinitrobenzene may be readily determined, the amount of the *m*-compound being estimated by difference.

The following conclusions are derived from the quantitative study of the product of nitration: (1) The nitration of nitrobenzene to dinitrobenzene by anhydrous nitric acid at 0° or 30° is practically quantitative, whilst at 40° and in the presence of sulphuric acid there is a tendency to form trinitrobenzene. (2) An elevation of temperature causes an increase in the amounts of *o*- and *p*-dinitrobenzene produced. (3) Excess of concentrated sulphuric acid diminishes the production of *o*-dinitrobenzene, but increases that of the *p*-isomeride to approximately the same extent. (4) The presence of water causes a considerable alteration in the velocity of the reaction, but does not affect the proportion of the isomerides. (5) The three isomerides are produced in the same proportions by weight throughout the reaction.

The amount of dinitrobenzene produced after a given time is found by taking the sp. gr. of the mixture of this product with unaltered nitrobenzene, a table having been previously constructed showing the connection between the sp. gr. of the solution and the quantity of dissolved dinitro-compounds. The authors' experiments indicate that the nitration of nitrobenzene cannot be expressed in the simple mathematical form of a bimolecular reaction. The equation would only apply to the case of infinite dilution, and, moreover, the products of the reaction,

water and dinitrobenzene, exercise a very marked disturbing influence.  
G. T. M.

**General Method for Preparing Sulphonic Derivatives by Means of Disulphides.** By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1900, 19, 111—114. Compare this vol., i, 226).—A preliminary communication dealing with the action of an alcoholic solution of sodium disulphide on certain aromatic nitro-compounds. *o*-Chloronitrobenzene and its bromine analogue are readily converted into 1 : 1'-dinitrodiphenyl disulphide, the latter substance, on oxidation, yielding *o*-nitrobenzenesulphonic acid. Sodium disulphide eliminates one atom of the halogen from 1 : 4 : 2-dichloronitrobenzene, 1 : 2 : 4-chlorodinitrobenzene, and the corresponding bromo-compounds, giving rise to aromatic disulphides which yield sulphonic acids on oxidation. Benzyl chloride and its *o*-nitro-derivative also yield disulphides, but these substances, when oxidised by nitric acid, are principally converted into carboxyl compounds. Allyl bromide and ethylene bromide also react with sodium disulphide, the compound derived from the latter yielding ethylenedisulphonic acid on oxidation. Sodium chloroacetate forms the disulphide  $S_2(CH_2 \cdot CO_2Na)_2$ , from which sulphoacetic acid may be prepared.  
G. T. M.

**The Number of Isomeric Naphthalene Derivatives.** By HERMANN REY (*Ber.*, 1900, 33, 1910—1917).—This paper contains a complete list of the number of possible isomerides derivable from naphthalene by substitution of similar or dissimilar radicles for the hydrogen atoms.  
J. J. S.

**Action of Nitrous Acid on Ethyl Anilinomalonate.** By RICHARD SYDNEY CURTISS (*Amer. Chem. J.*, 1900, 23, 509—512).—By the action of nitrous acid on ethyl anilinomalonate suspended in water, an amber-coloured *oil* is produced, to which the constitution  $OH \cdot \overset{\text{NPh}}{\underset{|}{N}} > C(CO_2Et)_2$  is assigned; it does not give Liebermann's

nitroso-reaction, readily decomposes with loss of nitrous oxide, and has marked acid properties; the yellow, crystalline *potassium* salt decomposes at 118°, and the *sodium* salt at 118—122°. Acetic anhydride gave, in one instance, a substance melting at 114°, and of mol. wt. about 300, but in a second experiment a substance melting at 111° and of mol. wt. 222.  
T. M. L.

**Behaviour of Phenylcarbimide with Ethyl Acetoacetate.** By WILHELM DIECKMANN (*Ber.*, 1900, 33, 2002—2005).—Ethyl acetoacetate reacts at the ordinary temperature with phenylcarbimide to form *ethyl acetylmalonanilate*,  $NHPh \cdot CO \cdot CHAc \cdot CO_2Et$ , which crystallises in colourless, glassy prisms or thick tablets melting at 57—58°. The formation of this compound from the ester throws some doubt on the trustworthiness of phenylcarbimide as a reagent for characterising the enolic form of tautomeric compounds.  
R. H. P.

**Constitution of Di-*p*-bromobenzylecyanamide.** By C. LORING JACKSON and R. W. FULLER (*Amer. Chem. J.*, 1900, 23, 494—500).—*Di-p*-bromobenzylecyanamide,  $CN \cdot N(CH_2 \cdot C_6H_4Br)_2$ , prepared by the



action of *p*-bromobenzyl bromide on silver cyanamide, melts at 133°, crystallises from benzene in flat, white needles, dissolves in most organic solvents, but only slightly in water, shows a normal molecular weight in benzene solution by the cryoscopic method, does not form a salt with hydrogen chloride, and does not polymerise when heated alone, or with water, alkali hydroxides, or ammonia; it is not readily hydrolysed by hydrochloric acid, but with sulphuric acid it is converted to di-*p*-bromobenzylamine, ammonia, and carbon dioxide. The constitution of the cyanamide is thus established, and serves to confirm Fileti and Schiff's conclusion (*Annalen*, 1854, 90, 95) that the dialkylcyanamides are derived from  $\text{NH}_2 \cdot \text{CN}$ , and not from  $\text{NH}:\text{C}:\text{NH}$ .  
T. M. L.

**Action of Cyanogen on Aromatic Amines.** By WILHELM MEYER (*J. pr. Chem.*, 1900, [ii], 61, 449—476).—By the action of acetyl chloride on a solution in pyridine of the additive product,  $\text{C}_{14}\text{H}_{14}\text{N}_2$ , of cyanogen and aniline, a polymeric *acetyl* derivative,  $\text{C}_{30}\text{H}_{30}\text{ON}_8$ , is produced, which forms violet crystals, melts at 205—207°, forms salts with acids, dissolves in organic solvents, but not in water, and is somewhat unstable; the *hydrochloride*,  $\text{C}_{30}\text{H}_{30}\text{ON}_8 \cdot 2\text{HCl}$ , is a dark, amorphous precipitate which has a slight dyeing power, and is reduced by iron filings and acetic acid to a leuco-compound which oxidises again on exposure to air. Benzoyl chloride gives an *anhydro-benzoyl* derivative,  $\text{C}_{21}\text{H}_{16}\text{N}_4$ , which crystallises from alcohol in minute, red needles, melts at 192—193°, has slight tinctorial properties, and is perhaps an imidazole derivative.

'Cyananiline' does not interact with ethyl orthoformate, and therefore probably does not contain a  $-\text{NH}_2$  group. It has been prepared by the action of mercuric oxide on an alcoholic solution of aniline and dithio-oxamide, and identified by means of the acetyl and benzoyl derivatives already described. The amount of 'cyanotriphenylguanidine,'

$\text{NPh}:\text{C} < \begin{matrix} \text{NPh}:\text{C}:\text{NH} \\ \text{NPh}:\text{C}:\text{NH} \end{matrix}$  obtained as a bye-product in the action of cyanogen on aniline, is only very small when the cyanogen is in excess.

'Cyano-*o*-toluidine' gives an *acetyl* derivative,  $\text{C}_{34}\text{H}_{38}\text{ON}_8$ , and *hydrochloride*,  $\text{C}_{34}\text{H}_{38}\text{ON}_8 \cdot 2\text{HCl}$ , analogous to those derived from 'cyananiline.'

'Cyano-*p*-anisidine,'  $[-\text{C}(\text{NH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}]_2$ , prepared by the action of cyanogen on *p*-anisidine, crystallises from alcohol in silvery flakes, melts at 207—209°, and forms a *hydrochloride*,  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4 \cdot 2\text{HCl}$ ; a *guanidine* derivative,  $\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_6$ , is also produced, which crystallises from alcohol in minute, yellow needles, melts with frothing at 154°, is a stronger base than the corresponding aniline derivative, and forms sparingly soluble red salts even with organic acids.

'Cyano-*o*-anisidine' crystallises in long prisms and melts at 205—207°; the *guanidine* derivative is only produced in small quantities, melts at 152°, and resembles the *o*-compound.

'Cyano-*p*-phenetidine,'  $\text{C}_2(\text{NH})_2(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$ , resembles 'cyananiline,' melts at 208—210°, and gives oxalphenetide when acted on by nitrous acid; the yellow *guanidine* derivative,  $\text{C}_{27}\text{H}_{29}\text{O}_2\text{N}_5$ , melts

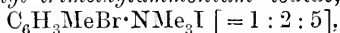
at 139—141°, forms a red *acetate* melting at 195—200°, and a red *hydrochloride*.

The only product of the action of cyanogen on  $\beta$ -naphthylamine is 'cyanotrinaphthylguanidine,' which is a yellow substance melting at 225—226°; it forms red salts, most of which are hydrolysed by adding much water; by boiling hydrochloric acid, it is hydrolysed into ammonia,  $\beta$ -naphthylamine, and oxalic acid.

'Cyanobenzidine' *platinichloride*,  $(C_{26}H_{24}N_6)_2 \cdot H_2PtCl_6$ , has been prepared and analysed, although all the salts are extremely unstable. When boiled with dilute sodium hydroxide, 'cyanobenzidine' is decomposed into benzidine, and a substance,  $C_{14}H_{12}N_4$ , which separates from toluene in white crystals, melts at 200°, and is regarded as 'dicyanobenzidine'; the further decomposition into benzidine, ammonia, and oxalic acid only takes place with difficulty.

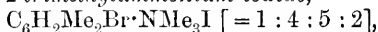
Dianisidine gives a red *compound*,  $(C_{14}H_{16}O_2N_2)_2(CN)_2$ , similar to 'cyanobenzidine.'  
T. M. L.

**Formation of Quaternary Ammonium Compounds in the case of Brominated Homologues of Aniline.** By EMIL FISCHER and ADOLF WINDAUS (*Ber.*, 1900, 33, 1967—1975. Compare this vol., i, 224).—5-Bromo-o-tolyl trimethylammonium iodide,



crystallises from water in silky needles and decomposes at 178°. The 1 : 3 : 6-*compound* crystallises in flakes and decomposes at 176—177°. The 1 : 4 : 3-*compound* (Pesci, *Gazzetta*, 1898, 28, ii, 109) decomposes at 189—192°.

5-Bromo-p-xylol-2-trimethylammonium iodide,



crystallises from water in four- or eight-sided flakes and decomposes at 188°. The 1 : 3 : 6 : 4-*compound* crystallises in long needles and decomposes at 200—201°. 5-Bromo-4-dimethylamino-*m*-xylene does not give a methiodide, in accordance with the rule that quaternary compounds are not formed where the two ortho-positions relatively to the amino-group are occupied. By the action of bromine on *as-m*-xylidine in presence of a large excess of cold hydrochloric or hydrobromic acid, a yellowish-red, crystalline mass is produced which has the composition  $C_8H_{10}NBr \cdot HBr$ , and probably contains a bromine atom in the amino-group, since the whole of the bromine is removed by sulphurous acid; on warming with hydrochloric acid, the bromine passes into the nucleus. 5-Bromo-1 : 3 : 4-xylidine (compare Vaubel, *Abstr.*, 1896, i, 646) crystallises from light petroleum in prisms and melts at 46—47°; the *acetyl* derivative crystallises from alcohol in prisms and melts at 197°; the constitution of the base has been established by converting it into a bromoxylene, which gave mesitylenic acid when acted on by sodium and ethyl chlorocarbonate. (4 or 5)-Bromo-1 : 3 : 2-xylidine, prepared in a similar way from the corresponding xylidine, crystallises from light petroleum in prisms and melts at 49—50°; the *acetyl* derivative crystallises from alcohol in prisms and melts at 197° (corr.); the bromine in the base is probably in the para-position to the amino-group, but this has not been proved.

Bromomesidine [ $Me_3 : NH_2 : Br = 1 : 3 : 5 : 2 : 4$ ], prepared in a similar

way from mesidine, crystallises from light petroleum in transparent tablets and melts at  $39^{\circ}$ . In *p*-xylidine and the three toluidines, the method of brominating here described does not give such good results, and it is better to brominate the formyl or acetyl derivative. *Bromo-p-xylidine* crystallises from light petroleum in needles and melts at  $96^{\circ}$ ; the *formyl* derivative crystallises from alcohol in long prisms and melts at  $148^{\circ}$ ; the position of the bromine atom has not been determined.

T. M. L.

**Quinquevalent Nitrogen.** By WILHELM VAUBEL (*Ber.*, 1900, 33, 1713—1714).—A claim for priority (compare Lachman, this vol., i, 380).

T. M. L.

**New Hydroxylamine Derivatives of Formic Acid.** By GEORG SCHROETER and M. PESCHKES (*Ber.*, 1900, 33, 1975—1987. Compare Abstr., 1898, i, 623).—*α*-Benzylhydroxylamine, when heated with ethyl formate at  $160^{\circ}$  in sealed tubes, yields an oil boiling at  $175$ — $182^{\circ}$  under 18 mm. pressure and benzaldoxime-O-benzyl ether. The sodium compound of benzaldoxime and *p*-nitrobenzyl chloride in alcoholic solution yield *benzaldoxime-p-nitrobenzyl ether*, which forms yellow crystals melting at  $60$ — $61^{\circ}$ , and is not affected by hydrolytic agents. *p*-Chlorobenzylhydroxylamine hydrochloride, obtained by the action of hydrochloric acid on *p*-chlorobenzylacetoxime, which is formed by the action of *p*-chlorobenzyl chloride on sodium acetoxime, crystallises in silvery, thin leaflets, sublimes without melting, and, when mixed with a solution of potassium cyanate, forms *p-chlorobenzyl-oxy-carbamide*, which crystallises in white leaflets melting at  $155$ — $156^{\circ}$ . The *base*, obtained by treating the hydrochloride with potassium hydroxide, boils at  $127.4$ — $128.2^{\circ}$  under 17 mm. pressure and solidifies to a mass of hard, clear crystals, which melt at  $38^{\circ}$ . *p*-Bromobenzylhydroxylamine, obtained in an analogous manner to the chloro-derivative, boils at  $133.5^{\circ}$  under 10 mm. pressure, and crystallises in long, glassy needles which melt at  $36$ — $37^{\circ}$ ; *p*-bromobenzyl-oxy-carbamide melts at  $157$ — $158^{\circ}$ ; *p*-chlorobenzaldoxime *p*-chlorobenzyl ether and *p*-bromobenzaldoxime *p*-bromobenzyl ether, obtained as bye-products in the preparation of the above compounds, crystallise in colourless needles and melt respectively at  $114^{\circ}$  and  $130^{\circ}$ .

*Formhydroxamoxime dibenzyl ether*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}:\text{CH}\cdot\text{NH}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , obtained by the action of *α*-benzylhydroxylamine on formimidoether hydrochloride, crystallises in clusters of needles which melt at  $42^{\circ}$ , and forms a *hydrochloride* which is a colourless, microcrystalline powder. *Formhydroxamoxime di-p-chlorobenzyl ether*, obtained in a similar manner from *p*-chlorobenzylhydroxylamine, crystallises in small, lustrous, white needles which melt at  $92.5$ — $93.4^{\circ}$ ; it forms a colourless, crystalline *hydrochloride* and an *acetyl* derivative, which melts at  $102$ — $103.4^{\circ}$ , and does not form a hydrochloride. *Formhydroxamoxime di-p-bromobenzyl ether* crystallises in small needles which melt at  $100^{\circ}$ , forms a colourless *hydrochloride*, and an *acetyl* derivative which crystallises in matted needles melting at  $94$ — $95^{\circ}$ .

R. H. P.

**Constitution of *iso*Purpuric Acid.** By RUDOLF NIETZKI and WILHELM PETRI (*Ber.*, 1900, 33, 1788—1797).—*iso*Purpuric acid is

best prepared by the interaction of aqueous potassium cyanide with picric acid at a temperature not exceeding  $35^{\circ}$ , rather than at  $100^{\circ}$  as stated by Hlasiwetz (*Annalen*, 1859, 110, 289); the facts which follow show that it is a *dicyanopicramic acid* (4:6-dinitro-2-amino-3:5-dicyanophenol).

When dilute hydrochloric acid is added to potassium *isopurpurate* suspended in glacial acetic acid, the acid *potassium* salt,  $C_8H_6O_6N_6K$ , of *dicyanodinitrohydroxydiazobenzene*,  $OH \cdot C_6(NO_2)_2(CN)_2 \cdot N:N \cdot OH$ , separates in beautiful, golden needles, which can be dried at  $100^{\circ}$  without decomposition, but explode with great violence at about  $210^{\circ}$ ; on dissolving it in aqueous potassium carbonate, the normal *potassium* salt,  $C_8O_6N_6K_2$ , separates in brownish-yellow prisms; the acid *sodium* salt,  $C_8HO_6N_6K$ , and the normal *barium* salt,  $C_8O_6N_6Ba + H_2O$ , were also prepared. The parent substance,  $C_8O_6N_6H_2$ , separates in yellow needles on dissolving the foregoing salts in concentrated nitric acid; it is very soluble in water, and is remarkable in that it is only slightly explosive, and, unlike diazo-compounds, fails to condense with amines and phenols.

On reducing the foregoing diazo-salts in the cold with stannous chloride dissolved in dilute hydrochloric acid, slender, red needles of what is apparently the corresponding *hydrazine* are obtained, although the substance fails to give the usual hydrazine reactions; if the diazo-salts are reduced by a warm solution of stannous chloride in concentrated hydrochloric acid, 5-cyano-2:4:6-triamino-3-hydroxybenzamide is obtained, owing to one of the cyano-groups having undergone partial hydrolysis. The base yields a crystalline *hydrochloride*, which loses its hydrogen chloride completely on exposure to air; it is readily oxidised by manganese dioxide in alkaline solution to the *quinoneimide*,  $NH \cdot C_6O(NH_2)_2(CN) \cdot CO_2H$ , of *cyanodiaminobenzoic acid*; this forms dark yellow needles, yields copper-red, crystalline *sodium* and *potassium* salts, and is reduced by stannous chloride in hydrochloric acid to 5-cyano-2:4:6-triamino-3-hydroxybenzoic acid, which is sparingly soluble in water, is easily oxidisable, and was analysed in the form of its *triacetyl* derivative,  $C_8H_5N_4O_3(OAc)_3$ . The quinoneimide interacts with hydroxylamine to form an *oxime*, the *potassium* salt of which,  $NH \cdot C_6(NH_2)_2(CO_2K)(CN):N \cdot OH + \frac{1}{2}H_2O$ , forms dark red crystals, and, on reduction, yields 5-cyano-2:3:4:6-tetraminobenzoic acid, which rapidly oxidises in the air.

Attempts to hydrolyse the foregoing derivatives of *m*-cyanobenzoic acid to the corresponding *isophthalic* acids by means of hydrochloric or sulphuric acid failed. On warming the quinoneimide of cyanodiaminobenzoic acid, however, with aqueous potassium hydroxide on the water-bath and adding hydrochloric acid, the acid *potassium* salt,  $C_8H_6O_3N_3K$ , of the *quinoneimide* of *diaminoisophthalic acid*,  $O \cdot C_6(NH_2)_2(CO_2H)_2:NH$  [ $= 1:2:6:3:5:4$ ], is obtained as a vermilion, crystalline precipitate. The corresponding acid could not be isolated, since, on dissolving the salt in concentrated sulphuric acid, the *anhydride*,  $C_8H_5O_4N_3$ , separates in reddish-yellow crystals. On reduction with stannous chloride, the quinoneimide yields 2:4:6-triamino-5-hydroxyisophthalic acid, the *tetracetyl* derivative of which melts at  $208^{\circ}$ . On reducing the *oxime* of the quinoneimide of diamino-

*isophthalic acid* with stannous chloride and hydrochloric acid, *tetramino-isophthalic acid* is obtained, which reddens in the air, owing to oxidation occurring.  
W. A. D.

**Action of Nitric Acid on Trichloroguaiacol.** By H. COUSIN (*Compt. rend.*, 1900, 131, 53—55. Compare this vol., i, 179).—Tetrachloroguaiacol, when treated with nitric acid, yields tetrachloro-o-quinone, and a similar result is obtained with tetrabromoguaiacol; the reaction with trichloroguaiacol takes an altogether different course.

The *quinone*,  $C_{13}H_5O_4Cl_3$ , is produced by the action of nitric acid on trichloroguaiacol dissolved in glacial acetic acid; it crystallises in reddish-yellow lamellæ melting at  $158-162^\circ$ , and separates from benzene solutions in prismatic crystals containing 1 mol. of the solvent. The corresponding *quinol*,  $C_{13}H_7O_4Cl_3$ , is readily obtained by the action of sulphurous acid on the quinone; it separates from benzene in colourless, prismatic crystals, which darken on exposure to the air and melt at  $166-167^\circ$ . Its alcoholic solution develops a green coloration with ferric chloride, the colour changing to violet on the addition of alkali. When subjected to Zeisel's method for the determination of methoxyl, the quinone yields 1 mol. of methyl iodide; on distilling it with zinc dust, diphenyl is obtained.

The reaction with nitric acid probably takes place in the following manner. Two mols. of trichloroguaiacol condense, losing 1 mol. of hydrogen chloride, one methyl group is removed by hydrolysis, and the product simultaneously undergoes oxidation. The quinone thus produced should have one or other of the following constitutions:  $O:C_6Cl_3(OMe) \cdot C_6HCl_2(OH):O$  or  $O:C_6HCl_2(OMe) \cdot C_6Cl_3(OH):O$ .

G. T. M.

**Synthesis of Dimethylmorphol and of *iso*Methylmorphol.** By ROBERT PSCHORR and C. SUMULEANU (*Ber.*, 1900, 33, 1810—1823. Compare Vongerichten, this vol., i, 248.)—*α-Phenyl-2-nitro-3:4-dimethoxycinnamic acid*,  $NO_2 \cdot C_6H_2(OMe)_2 \cdot CH: CPh \cdot CO_2H$ , is obtained when *o*-nitrovanillin methyl ether, melting at  $55-56^\circ$  (this vol., i, 178), is heated with anhydrous sodium acetate and acetic anhydride for some 24 hours; it crystallises from dilute alcohol in yellowish needles melting at  $225^\circ$  (corr.), and is sparingly soluble in ether, benzene, or chloroform. A small amount of *2-nitro-3:4-dimethoxystilbene* is always obtained as a by-product in the preparation of the cinnamic acid; it crystallises from hot alcohol in lemon-yellow, six-sided plates melting at  $122-123^\circ$ , and is readily soluble in ether, acetone, or hot acetic acid; it cannot be obtained directly from the acid by the elimination of carbon dioxide. *α-Phenyl-2-amino-3:4-dimethoxycinnamic acid*, obtained by reducing an ammoniacal solution of the nitro-acid with ferrous sulphate, crystallises in flat, yellowish prisms melting at  $179^\circ$  (corr.) and readily soluble in ether, acetone, acetic acid, chloroform, or hot benzene. When this acid is heated for some time with dilute sulphuric acid or more readily with acetic anhydride and a trace of sulphuric acid, it is converted into *2-phenyl-7:8-dimethoxycarbostyryl*, which crystallises from hot toluene in colourless, flat needles melting at  $247-248$  (corr.). *3:4-Dimethoxyphenanthrene-9-carboxylic acid*, formed when the

diazotised amino-acid is treated with molecular copper, crystallises from hot alcohol in small, yellowish needles melting at  $227-228^{\circ}$  (corr.); the *ferric* salt forms slender, yellow needles, and the *copper*, *lead*, and *mercuric* salts amorphous precipitates. When the acid is distilled under 300 mm. pressure, it is converted into 3:4-dimethoxyphenanthrene; this distils at  $298-303^{\circ}$  under 112 mm. pressure, crystallises from dilute alcohol in colourless, glistening, quadratic plates melting at  $44^{\circ}$ , and is in all respects identical with Vongerichten's dimethylmorphol (compare following abstract). The *picrate* forms ruby-red crystals melting at  $105-106^{\circ}$ , and the *dibromo*-derivative,  $C_{16}H_{12}O_2Br_2$ , needles melting at  $124-125^{\circ}$ .

When dimethylmorphol is hydrolysed with acetic and concentrated hydriodic acids, the product is not morphol, but 3-hydroxyphenanthrene; this crystallises in needles melting at  $118-119^{\circ}$ , and yields an *acetyl* derivative melting at  $114-115^{\circ}$ .

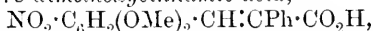
*α-Phenyl-2-nitro-4-acetoxy-3-methoxycinnamic acid*, obtained from *o*-nitroacetylvanillin, sodium phenylacetate, and acetic anhydride, crystallises from toluene in needles melting at  $178^{\circ}$  (corr.) and readily soluble in most organic solvents. The corresponding *amino*-acid could not be obtained in a pure state, as it is readily transformed into 3-phenyl-7-hydroxy-8-methoxy-2-carbostyryl, which crystallises in colourless needles melting at  $243^{\circ}$  (corr.). 3-Hydroxy-4-methoxyphenanthrene-9-carboxylic acid could not be obtained pure; it forms brown needles melting at  $214-216^{\circ}$  (corr.); when heated with 15 times its weight of glacial acetic acid at  $210-215^{\circ}$  for 10 hours, it yields 3-hydroxy-4-methoxyphenanthrene (isomethylmorphol) as an oil the *acetyl* derivative of which melts at  $93-94^{\circ}$ .  
J. J. S.

**Identity of Dimethylmorphol and of 3:4-Dimethoxyphenanthrene.** By EDUARD VONGERICHTEN (*Ber.*, 1900, **33**, 1824—1825. Compare preceding abstract).—When acetylmethylmorphol is hydrolysed with sodium methoxide in the absence of air, and then heated with methyl iodide also in the absence of air, a dimethylmorphol is obtained which is identical with Pschorr's 3:4-dimethoxyphenanthrene.  
J. J. S.

**Synthesis of 4-Hydroxyphenanthrene.** By ROBERT PSCHORE and BERNHARD JAECKEL (*Ber.*, 1900, **33**, 1826—1829).—*α-Phenyl-2-nitro-3-methoxycinnamic acid*,  $NO_2 \cdot C_6H_3(OMe) \cdot CH:OPh \cdot CO_2H$ , obtained from 2-nitro-3-methoxybenzaldehyde (*Abstr.*, 1889, 1169), sodium phenylacetate, and acetic anhydride, crystallises in colourless plates melting at  $226-227^{\circ}$  (corr.), dissolves sparingly in toluene, and is insoluble in light petroleum; the *calcium*, *barium*, *mercuric*, *copper*, and *plutinic* salts are described. The corresponding *amino*-acid crystallises from alcohol in lemon-yellow, felted needles melting at  $208-209^{\circ}$  (corr.), and is readily soluble in most organic solvents with the exception of light petroleum or water. The *ammonium*, *calcium*, and *silver* salts are described. When the acid is diazotised and treated with finely-divided copper, it yields 4-methoxyphenanthrene-9-carboxylic acid, which crystallises from toluene in slender needles melting at  $224^{\circ}$  (corr.), and only sparingly soluble in the usual solvents. 4-Methoxyphenanthrene, obtained by distilling the carboxylic acid

under 150 mm. pressure, crystallises from dilute alcohol in glistening plates melting at  $68^{\circ}$ ; it yields a *picrate*,  $C_5H_{12}O, C_6H_3O_7N_3$ , crystallising in red needles and melting at  $187-188^{\circ}$  (corr.); when hydrolysed and heated with acetic anhydride, it yields 4-*acetoxypheanthrene*,  $C_{16}H_{12}O_2$ , which crystallises from dilute alcohol in colourless plates melting at  $58-59^{\circ}$ . 4-*Methoxylibromophenanthrene*,  $C_{15}H_{10}OBr_2$ , crystallises in colourless needles melting at  $152^{\circ}$  (corr.), and 4-*methoxydibromophenanthraquinone*,  $C_{15}H_8O_3Br_2$ , crystallises in reddish-yellow needles melting at  $160^{\circ}$ .  
J. J. S.

**Synthesis of 2:3-Dimethoxyphenanthrene.** By ROBERT PSCHORR and WALTER BUCKOW (*Ber.*, 1900, 33, 1829—1832).—*α-Phenyl-2-nitro-4:5-dimethoxycinnamic acid*,



obtained by the condensation of sodium phenylacetate, *s*-nitrovanillin methyl ether, and acetic anhydride, crystallises from alcohol in yellow, felted needles melting at  $219^{\circ}$  (corr.); it dissolves readily in most organic solvents, sparingly in benzene or ether, and is practically insoluble in light petroleum. The *silver, lead, platinum, copper, and ferric* salts are described. The corresponding *amino-acid* crystallises from alcohol in yellow, hair-like needles melting at  $209^{\circ}$  (corr.), and is insoluble in water or light petroleum; its *hydrochloride, nitrate, and sulphate* crystallise in needles, and the sulphate is somewhat sparingly soluble. When the amino-acid is heated with acetic anhydride and a little sulphuric acid, it is converted into its inner anhydride, 2-*phenyl-5:6-dimethoxy-1-carbostyryl*, which crystallises from alcohol in long, colourless needles melting at  $261^{\circ}$  (corr.).

2:3-*Dimethoxyphenanthrene-9-carboxylic acid*, formed when the amino-acid is diazotised and treated with copper powder, crystallises from alcohol in needles melting at  $270^{\circ}$  (corr.), and is insoluble in water or light petroleum; its *silver, barium, lead, and platinum* salts form colourless, amorphous precipitates. When the acid is distilled under 150—200 mm. pressure, a 40—45 per cent. yield of 2:3-*dimethoxyphenanthrene* is obtained; this crystallises from dilute alcohol in plates melting at  $131^{\circ}$  (corr.), and is readily soluble in most organic solvents. The *picrate* forms long, yellowish-red needles melting at  $127-128^{\circ}$ , and is readily soluble in alcohol. *Dimethoxydibromophenanthrene*,  $C_{16}H_{12}O_2Br_2$ , crystallises from acetic acid in needles melting at  $160^{\circ}$  (corr.).

2:3-*Dimethoxyphenanthraquinone* forms dark red needles melting at  $304^{\circ}$  (corr.), and *dimethoxydibromophenanthraquinone* brownish-yellow crystals melting at  $158^{\circ}$ .  
J. J. S.

**An Aromatic Alcohol in German Oil of Roses.** By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1900, 33, 1720—1724).—On distilling the blossoms with water, oil of roses and 'rose-water' are obtained, and the latter is redistilled to obtain a further quantity of oil of roses, leaving behind an aqueous residue. By extracting this residue with ether, an oil was obtained (200 grams from 800 kilograms of the water) which was found to consist of benzylcarbinol (*β*-phenylethyl alcohol); when oxidised with chromic acid, this gave as the chief product *β*-phenylethyl phenylacetate,  $CH_2Ph \cdot CO_2 \cdot CH_2 \cdot CH_2Ph$ , which

crystallises from methyl alcohol in long needles, melts at  $28^{\circ}$ , boils at  $330^{\circ}$  with slight decomposition, and is hydrolysed by alcoholic potash to phenylacetic acid.

By a similar method, the presence of phenylethyl alcohol was detected in 'rose-water,' and, in smaller quantities, in German oil of roses. The alcohol was prepared by Radziszewski (Abstr., 1876, ii, 78) by reducing phenylacetaldehyde with sodium amalgam, but a better yield is obtained by reducing with zinc dust and acetic acid; the pure alcohol boils at  $219^{\circ}$ , has a sp. gr. 1.0235 at  $15^{\circ}$ , and is oxidised to the ether melting at  $28^{\circ}$ . T. M. L.

***o*-Methoxyphenyltrichloromethylcarbinol.** By S. LEBEDEF (J. Russ. Phys. Chem. Soc., 1900, 32, 197—207).—*o*-Methoxyphenyltrichloromethylcarbinol,  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , formed by the action of potassium hydroxide and chloroform on *o*-methoxybenzaldehyde, is obtained either as glistening crystals melting at  $53^{\circ}$ , or as a thick, reddish-yellow liquid boiling at  $174^{\circ}$  under 12 mm. pressure, which has a sp. gr. 1.4473 at  $0^{\circ}/0^{\circ}$ , dissolves readily in ether and slightly in light petroleum, and absorbs moisture from the air with development of a brownish coloration. Its *acetyl* derivative,  $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Cl}_3$ , separates from alcohol in well-developed, monoclinic crystals melting at  $58^{\circ}$  and exhibiting prismatic hemihedrism [ $a : b : c = 0.9370 : 1 : 0.6036$ ,  $\beta = 98^{\circ}48'$ ]. The acute bisectrix makes an angle of about  $22.5^{\circ}$  with the *a* axis and about  $14.5^{\circ}$  with the *c* axis; the crystals are optically negative and show horizontal dispersion,  $\rho > v$ . By treating an alcoholic solution of this *acetyl* derivative with zinc, two products are obtained:

(1)  *$\beta$ -Dichloro-o-methoxystyrene*,  $\text{CCl}_2 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , is a colourless liquid with a pleasant, though weak, odour; it boils at  $123$ — $125^{\circ}$  under 12 mm. pressure, and has a sp. gr. 1.2899 at  $0^{\circ}/0^{\circ}$  and 1.2701 at  $20^{\circ}/0^{\circ}$ .

(2) *Acetyl-o-methoxyphenyldichloromethylcarbinol*,  
 $\text{CHCl}_2 \cdot \text{CH}(\text{OAc}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ ,

separates from ether in crystals melting at  $108^{\circ}$ , and has the normal molecular weight in freezing benzene.

*o*-Methoxyphenylacetic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared by the action of alcoholic potash (4 mols.) on *o*-methoxydichlorostyrene (1 mol.), separates from ether in crystals which melt at  $123^{\circ}$  and are readily soluble in boiling water. T. H. P.

**Synthesis of Styryltrichloromethylcarbinol and the Action of 5 per cent. Aqueous Potassium Hydroxide on it.** By A. DROGLAUF (J. Russ. Phys. Chem. Soc., 1900, 32, 216—230).—*Styryltrichloromethylcarbinol*,  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH} : \text{CHPh}$ , obtained by the action of potassium hydroxide and chloroform on cinnamaldehyde, crystallises from light petroleum in bushy aggregates of slender needles melting at  $67^{\circ}$ ; it dissolves readily in ether, alcohol, chloroform, benzene, or carbon disulphide, less so in light petroleum, and is completely insoluble in water. By heating with water in sealed tubes at  $180^{\circ}$ , it yields  *$\beta$ -benzoylpropionic acid*. Its *acetyl* derivative,  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{Cl}_3$ , is a thick, faintly-yellow liquid boiling at  $160$ — $165^{\circ}$  under 20 mm. pressure. By the action of cold 5 per cent. aqueous potassium hydroxide, styryltrichloromethylcarbinol is converted into



$\beta$ -benzoylpropionic acid which, when heated in molecular proportion with phenylhydrazine, gives the anhydride of its phenylhydrazone, obtained by Fittig (*Annalen*, 1898, 299, 28).

With a cold 5 per cent. solution of sodium ethoxide, styryltrichloromethylcarbinol yields *phenylallenecarboxylic acid*,  $\text{CHPh}:\text{C}:\text{CH}\cdot\text{CO}_2\text{H}$ , which was obtained as a pale yellow resin; the *silver* salt was prepared. On treatment with cold 5 per cent. aqueous potassium hydroxide, this acid is converted into  $\beta$ -benzoylpropionic acid; it may hence be regarded as an intermediate product in the transformation of styryltrichloromethylcarbinol into  $\beta$ -benzoylpropionic acid by means of cold potassium hydroxide solution. T. II. P.

**Action of Anhydrous Nitric Acid on the Isomeric Chlorobenzoic Acids and their Derivatives.** By P. J. MONTAGNE (*Rec. Trav. Chim.*, 1900, 19, 46—78. Compare Taverne, *Abstr.*, 1898, i, 525, 586, 658, and Holleman, this vol., i, 387).—The *methylamide* of *o*-chlorobenzoic acid crystallises from dilute alcohol in monoclinic plates and melts at  $121\cdot5^\circ$ ; the *dimethylamide* is a liquid at the ordinary temperature, it boils at  $157\cdot5$ — $159^\circ$  under 14 mm. pressure, and solidifies at  $13\cdot5^\circ$ . *2-Chloro-5-nitrobenzoic chloride* boils at  $157$ — $158^\circ$  under 11 mm. pressure; the *methyl* ester of the corresponding acid crystallises from methyl alcohol in monoclinic needles and melts at  $73^\circ$ ; the *amide* forms monoclinic needles melting at  $178^\circ$ , the *methylamide* and *dimethylamide* melt at  $174^\circ$  and  $124\cdot5^\circ$  respectively.

The *methylamide* of *m*-chlorobenzoic acid crystallises from dilute alcohol in monoclinic needles melting at  $75^\circ$ , and separates from aqueous solutions in needles containing 1 mol. of the solvent; the *dimethylamide* forms rhombic plates and melts at  $61^\circ$ . *3-Chloro-6-nitrobenzoic chloride* boils at  $167^\circ$  under 17 mm. pressure, the corresponding *methyl* ester crystallises from methyl alcohol in monoclinic plates and melts at  $48\cdot5^\circ$ ; the *amide* forms triclinic needles melting at  $154^\circ$ ; the *methylamide* crystallises in white needles and melts at  $134^\circ$ ; the *dimethylamide* melts at  $104\cdot5^\circ$ . The *methylamide* of *p*-chlorobenzoic acid forms monoclinic needles and melts at  $161^\circ$ , the *dimethylamide*, crystallising in a similar form, melts at  $59^\circ$ .

*4-Chloro-3-nitrobenzoic chloride* melts at  $51^\circ$  and boils at  $170$ — $170\cdot5^\circ$  under 22 mm. pressure; the corresponding *methyl* ester forms white, monoclinic needles melting at  $83^\circ$ ; the *amide* melts at  $156^\circ$ , the *methylamide* at  $135\cdot5^\circ$ , and the *dimethylamide* at  $113\cdot5^\circ$ .

The methyl *o*-, *m*-, and *p*-chlorobenzoates, on nitration with anhydrous nitric acid at  $0^\circ$ , yield respectively the methyl 2:5-, 3:6-, and 4:3-chloronitrobenzoates. Under similar conditions, the *o*-, *m*-, and *p*-chlorobenzamides are converted respectively into 2:5-, 3:6-, and 4:3-chloronitrobenzamides, the ortho-compound being more readily nitrated than its isomerides. The nitration of the methylamides and dimethylamides of the chlorobenzoic acids at  $0^\circ$  gives rise to nitroderivatives containing the entering group in the same position as in the preceding examples, but in addition the *m*- and *p*-methylamides also yield methylnitramines,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NMe}\cdot\text{NO}_2$ , the *m* compound decomposing at  $148^\circ$  and the *p*-isomeride at  $90^\circ$ ; these nitramines

may also be prepared by the direct action of nitric acid on the corresponding chloronitromethylamides. When the nitration of the chlorobenzamides is carried out at the ordinary temperature, the nitrated amides first produced undergo hydrolysis and yield the corresponding chloronitrobenzoic acids; the methylamides undergo a similar change, giving rise to these nitrated acids, nitrous oxide, and methyl nitrate, whilst the dimethylamides also give rise to the same acids and dimethylnitramine. The orientation of the nitro-derivatives obtained as the chief products of the above-mentioned reactions is the same as that of the chloronitrobenzoic acids produced by the direct nitration of the chlorobenzoic acids.

G. T. M.

**Intramolecular Rearrangement.** By KARL AUWERS (*Ber.*, 1900, 33, 1923—1924. Compare Einhorn, this vol., i, 439).—*Dibromo-o-hydroxybenzylacetylanilide*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{N} \cdot \text{AcPh}$  [ $\text{OH} : \text{Br}_2 : \text{CH}_2 = 1 : 4 : 6 : 2$ ], is obtained when the acetyl derivative of dibromo-*o*-hydroxybenzyl bromide (*Annalen*, 1898, 302, 150) is warmed with aniline; it melts at  $152^\circ$ , is soluble in cold dilute alkalis, and may also be obtained by the action of acetic anhydride on dibromo-*o*-hydroxybenzylaniline. The isomeric meta- and para-compounds do not undergo similar changes.

J. J. S.

**Sodium Salts of the Amides.** By HENRY L. WHEELER (*Amer. Chem. J.*, 1900, 23, 453—471).—The amount of sodium salt formed by the action of sodium amalgam on a solution of an amide in boiling benzene does not depend in any regular way on the affinity constants of the acid and base from which the amide is derived. A disubstituted formamide gives a sodium derivative less readily than a mono-substituted formamide, and the inhibiting effect of a radicle is greater when it is attached to the CO group than when it is attached to the NH group, suggesting that the sodium of the salts is associated with oxygen and not with nitrogen. In contrast to oxindole and phthalimidine, benzoylbenzylamine is quite inert.

*o*-Toluamide forms a sodium salt somewhat less readily than benzamide, but trimethylbenzamide is only slightly less active in this respect than *o*-toluamide. As regards substitution in the amino-group, benzylbenzamide, methylbenzamide, and ethylbenzamide are practically inert, but benzanilide gives a considerable amount of sodium derivative.

*Sodium* derivatives of the following *amides* have been prepared and analysed; oxanilide, benzamide, oxindole, phthalimidine, *o*-formyltoluidide, *o*-toluamide, *a*-formylnaphthalide, *a*-naphthamide, 2 : 4 : 6-trimethylformylanilide, 2 : 4 : 6-trimethylbenzamide, and 2 : 4 : 6-tribromobenzamide.

It is suggested that the formation of sodium derivatives is conditioned by the presence of a trace of moisture and that an additive compound with sodium hydroxide is formed as an intermediate product; three such additive compounds have been prepared. 2 : 4 : 6-Trimethylbenzamide potassium hydroxide was prepared by shaking an ethereal solution of the amide with powdered potassium hydroxide; it is completely decomposed by water. 2 : 4 : 6-Tribromobenzamide sodium hydroxide,  $\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{NaOH}$ , was prepared by the action of

powdered sodium hydroxide on a solution of the amide in benzene, and is completely decomposed by water; the chloride, methyl ester, and dimethylamide do not combine with caustic alkalis.

*Thioacetanilide sodium hydroxide*,  $\text{C}_6\text{H}_5\cdot\text{NH}_2\cdot\text{NaOH}$ , was prepared in a similar manner, and when acted on by benzoyl chloride gave acetanilide and thiobenzoic acid, showing that it is probably a derivative of the formula  $\text{NHPh}\cdot\text{CMe}(\text{OH})\cdot\text{SNa}$ , and not a mere 'molecular compound.'

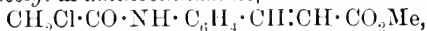
T. M. L.

**Action of Benzyl Cyanide on Ethyl Cinnamate.** By EMIL ERLÉNMEYER, jun. (*Ber.*, 1900, 33, 2006—2011).—The experiments of Walther and Schickler (*Abstr.*, 1897, i, 524) on the condensation of benzyl cyanide and ethyl cinnamate in the presence of sodium ethoxide have been repeated, and two new compounds isolated; one of these has the empirical formula  $\text{C}_{19}\text{H}_{19}\text{O}_2\text{N}$ , and crystallises in small, colourless needles melting at  $99-100^\circ$ , and the other has the formula  $\text{C}_{28}\text{H}_{25}\text{O}_3\text{N}$ , and crystallises in small, colourless needles melting at  $206-207^\circ$ . The paper concludes with a discussion of the probable formulæ of these compounds.

R. H. P.

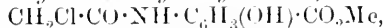
**New Drugs. Glyciny! Derivatives of the Esters of Aromatic Amino- and Hydroxyamino-acids.** By ALFRED EINHORN and MAX OPPENHEIMER (*Annalen*, 1900, 311, 154—178. Compare this vol., i, 439).—*Methyl chloroacetylanthranilate*,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , crystallises from absolute alcohol in slender needles and melts at  $98-99^\circ$ . *Methyl chloroacetyl-m-aminobenzoate* forms pale brown crystals and also melts at  $98-99^\circ$ . *Methyl chloroacetyl-p-aminobenzoate* separates from alcohol in white crystals and melts at  $138^\circ$ .

*Methyl chloroacetyl-m-aminocinnamate*,



crystallises in small needles and melts at  $122^\circ$ . *Methyl chloroacetyl-p-aminocinnamate* forms lustrous, pale brown needles and leaflets melting at  $155-156^\circ$ .

*Methyl 3-chloroacetylamino-o-hydroxybenzoate*,



crystallises in slender needles and melts at  $106^\circ$ .

*5-Chloroacetylamino-o-hydroxybenzoic acid*,  $\text{C}_6\text{H}_3\text{O}_4\text{NCl}\cdot\text{H}_2\text{O}$ , crystallises from glacial acetic acid in nodules and melts at  $233-234^\circ$ , when it decomposes; the *methyl* and *ethyl* esters melt at  $157^\circ$  and  $131.5^\circ$  respectively.

*Methyl 4-chloroacetylamino-m-hydroxybenzoate* melts at  $187-188^\circ$ , and *methyl 3-chloroacetylamino-p-hydroxybenzoate* melts at  $191-192^\circ$ .

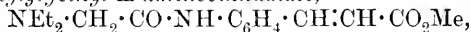
*Methyl methylglyciny!anthranilate*,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , is a yellow oil yielding a crystalline *hydrochloride* which melts at  $202^\circ$ . *Methyl ethylglyciny!anthranilate* is also an oil; the *hydrochloride*, which crystallises from acetone, melts at  $191^\circ$ , when it decomposes. The *hydrobromide* of methyl dimethylglyciny!anthranilate melts and decomposes at  $195^\circ$ ; the *hydrobromide* of methyl diethylglyciny!anthranilate melts at  $120^\circ$ .

*Methyl ethylglyciny!-m-aminobenzoate* melts at  $68-69^\circ$ ; the *hydrochloride* crystallises in small needles and melts at  $193-194^\circ$ . *Methyl*

*diethylglycynyl-m-aminobenzoate* is an oil yielding the *hydrochloride* which melts at 177°.

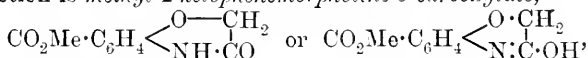
*Methyl methylglycynyl-p-aminobenzoate* crystallises from ethyl acetate in slender needles and melts at 108—109°; the *hydrochloride* melts at 225—226°. *Methyl ethylglycynyl-p-aminobenzoate* melts at 101—102°, and the *hydrochloride* at 218°. *Methyl diethylglycynyl-p-aminobenzoate* melts at 59—60°, the *hydrochloride* at 186—187°, and the *hydrobromide* at 170·5°.

*Methyl diethylglycynyl-m-aminocinnamate*,



is an oil forming the *hydrochloride*, which melts at 165°. *Methyl diethylglycynyl-p-aminocinnamate* is also an oil, yielding the *hydrochloride*, which crystallises in needles and melts at 188—189°.

*Methyl p-diethylglycynylamino-m-hydroxybenzoate*, prepared from methyl *p*-chloroacetylamino-*m*-hydroxybenzoate (*chloroacetylorthoform*) and diethylamine, crystallises from dilute alcohol in leaflets, and melts at 157—158°; the *hydrochloride* melts at 95—96°. The other product of the action is *methyl 2-ketophenemorpholine-5-carboxylate*,



which crystallises from glacial acetic acid in slender needles, dissolves sparingly in most solvents, and melts at 253°; the *acid* melts at 290°, and the *amide* at 270°.

*Methyl m-diethylglycynylamino-p-hydroxybenzoate*, prepared from methyl *m*-chloroacetylamino-*p*-hydroxybenzoate and diethylamine, crystallises from acetone in slender, lustrous leaflets and melts at 174·5°; the *hydrochloride* is very hygroscopic, and, after softening at 60—80°, melts at 162°. *Methyl 2-ketophenemorpholine-6-carboxylate* is also produced, and melts at 193—194°; the *acid* melts at 285°, and the *amide* crystallises in small, white leaflets.

*Methyl 3-diethylglycynylaminosalicylate*, obtained from methyl 3-chloroacetylamino-*o*-hydroxybenzoate and diethylamine, melts at 41—42°, and yields the *hydrochloride* melting at 75—76°. There is also produced *methyl 2-ketophenemorpholine-4-carboxylate*, which crystallises from methyl alcohol in needles and melts at 200—201°.

*Methyl 5-methylglycynylaminosalicylate* melts at 73—74°, and the *hydrochloride* melts and decomposes at 220°. *Methyl 5-ethylglycynylaminosalicylate* melts at 58—59°, and the *hydrochloride* at 225·5°. *Methyl 5-diethylglycynylaminosalicylate* (*nirvanine*) is a yellow oil forming a crystalline *hydrochloride* which melts and decomposes at 185°; the *aurichloride*, *platinichloride*, and *mercurichloride* contain 1H<sub>2</sub>O, and melt at 170—171°, 210°, and 150—151° respectively. The *amide* crystallises from benzene in white needles and melts at 144°. *Ethyl 5-diethylglycynylaminosalicylate* is an oil, and yields the *hydrochloride*, which melts at 198·5°, and in aqueous solution develops a violet coloration with ferric chloride.

M. O. F.

**Alkylthiosulphonated Ethyl Acetoacetate.** By JULIUS TROEGER and ERICH EWERS (*Arch. Pharm.*, 1900, 238, 309—320).—Thiosulphonates do not condense easily with chloroketones, but readily interact with ethyl  $\alpha$ -chloroacetoacetate. Potassium

benzenethiosulphonate forms *ethyl phenylthiosulphonacetoacetate*,  $\text{SO}_2\text{Ph}\cdot\text{S}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , which separates from alcohol in compact, white crystals and melts at  $55-56^\circ$ . *Ethyl p-tolylthiosulphonacetoacetate* separates from alcohol in large, glistening tablets and melts at  $62-63^\circ$ .

*Ethyl  $\beta$ -naphthylthiosulphonacetoacetate* separates from alcohol in well-formed crystals and melts at  $82^\circ$ . The  $\alpha$ -*naphthyl* compound separates from methyl alcohol in compact, glistening crystals and melts at  $89-90^\circ$ . All these compounds give a blood-red coloration with ferric chloride.

T. M. L.

**Oxidation of Anethole and Analogues (*iso*Safrole, *iso*-*Apiole*, &c.) containing Propenylic Side Chains.** By J. BOUGAULT (*Compt. rend.*, 1900, 130, 1766-1768).—The *aldehyde*,  $\text{C}_{10}\text{H}_{12}\text{O}_2$ , obtained by oxidising anethole in alcoholic solution with a mixture of mercuric oxide and iodine, is a colourless, highly refractive, inodorous liquid, volatile in steam and boiling at  $252-254^\circ$ ; it is almost insoluble in water or light petroleum, but dissolves readily in alcohol, ether, or chloroform.

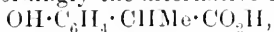
The *acid*,  $\text{C}_{10}\text{H}_{12}\text{O}_3$ , produced by shaking the aldehyde with moist silver oxide in the presence of sodium hydroxide solution, melts at  $57^\circ$ .

Since these substances result from the oxidation of the propenylic side chain of anethole, their constitutions may be represented provisionally by the following formulæ:  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_4\cdot\text{CHO}$  and  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_4\cdot\text{CO}_2\text{H}$ .

The *acids*,  $\text{C}_{10}\text{H}_{16}\text{O}_4$ ,  $\text{C}_{14}\text{H}_{14}\text{O}_4$ , and  $\text{C}_{12}\text{H}_{14}\text{O}_6$ , obtained by similar processes from *isosafrole*, *isomethyleugenol*, and *isoapiole* melt at  $80^\circ$ ,  $60^\circ$ , and  $97^\circ$  respectively.

G. T. M.

**Methoxyhydratropic Acid obtained by Oxidising Anethole; Identity of Phloretic and Hydroparacoumaric Acids.** By J. BOUGAULT (*Compt. rend.*, 1900, 131, 42-45. Compare preceding abstract).—Hydroparacoumaric acid has the constitution  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , having been synthesised from *p*-amino-cinnamic acid, and accordingly the alternative formula,



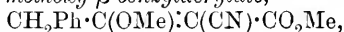
has hitherto been assigned to phloretic acid, its supposed isomeride. A comparative study of the derivatives of these acids shows unmistakably that the two substances are identical. It follows that their methyl derivatives, methoxyparacoumaric acid and methylphloretic acid, are also identical, having the formula  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ; the alternative formula,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , is therefore available for the new isomeric acid obtained by the author in oxidising anethole, and, accordingly, this compound is *methoxyhydratropic acid*; its aldehyde, formed as an intermediate product in the oxidation, consequently has the formula  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CHO}$ .

It is difficult to interpret these results on the assumption that anethole contains the straight chain  $\cdot\text{CH}\cdot\text{CHMe}\cdot$ ; if, however, this substituent group is a trimethylene residue,  $\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ , then a simple explanation of the oxidation becomes possible.

These remarks apply also to the acids and aldehydes derived from *isosafrole*, *isomethyleugenol*, and *isopiole*. G. T. M.

**Alkyl Salts of  $\alpha$ -Cyano- $\beta$ -alkyloxy- $\beta$ -phenyl- and - $\beta$ -benzyl-acrylic Acids.** By ALBIN HALLER and G. BLANC (*Compt. rend.*, 1900, 130, 1591—1595).—*Ethyl  $\alpha$ -cyano- $\beta$ -methoxy- $\beta$ -phenylacrylate*,  $\text{OMe} \cdot \text{CPh} : \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , obtained by the action of methyl iodide on ethyl argentocyanobenzoylacetate in presence of ether, forms white crystals which melt at  $106-107^\circ$ . The corresponding  *$\beta$ -ethoxy-acid* forms triclinic crystals which melt at  $86^\circ$ , and the  *$\beta$ -propoxy-acid* forms white crystals which melt at  $95-96^\circ$ . All three acids, when dissolved in alcohol and mixed with aqueous ammonia, yield one and the same amino-derivative, crystallising in white crystals melting at  $125^\circ$ , the amino-group having displaced the alkyloxy-group.

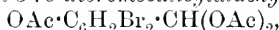
*Methyl  $\alpha$ -cyano- $\beta$ -methoxy- $\beta$ -benzylacrylate*,



and the corresponding  *$\beta$ -ethoxy-acid*, are oily compounds obtained by the action of methyl and ethyl iodides respectively on methyl argentocyanacetophenylacetate, and when treated with ammonia they both yield the same white, crystalline amino-derivative melting at  $101-102^\circ$ , in which the alkyloxy-group has been displaced by the amino-group.

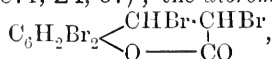
It would seem that, in the form of argentic derivatives, the alkyl salts of benzoyl- and cyanoacetyl-phenylacetic acids behave like argentic derivatives of the alkyl acetocyanacetates, the group  $\cdot \text{CO}(\text{CN}) \cdot \text{CH} \cdot \text{CO}_2\text{R}$  taking the form  $\cdot \text{C}(\text{CN})(\text{OH}) : \text{C} \cdot \text{CO}_2\text{R}$ , and the tautomerism being determined by the introduction of silver into the molecule. C. H. B.

**Tribromocoumarin and its Derivatives. II.** By HUGO SIMONIS and G. WENZEL (*Ber.*, 1900, 33, 1961—1967. Compare this vol., i, 231).—*Triacetyl-3:5-dibromosalicylaldehyde*,



prepared by the action of acetic anhydride on sodium 3:5-dibromosalicylaldehyde, crystallises from alcohol in colourless prisms and melts at  $103^\circ$ ; it is hydrolysed by boiling with dilute acids to 3:5-dibromoacetylsalicylaldehyde,  $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CHO}$ , which crystallises in long needles and melts at  $90^\circ$ . By the action of sodium acetate and acetic anhydride on 3:5-dibromosalicylaldehyde, 6:8-dibromo-

coumarin,  $\text{C}_6\text{H}_2\text{Br}_2 \cdot \begin{smallmatrix} \text{CH} : \text{CH} \\ \diagdown \quad \diagup \\ \text{O} - \text{CO} \end{smallmatrix}$  can be directly prepared (compare Perkin, this Journal, 1871, 24, 37); the *dibromide*,

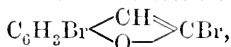


is formed very slowly by the action of bromine on dibromocoumarin dissolved in carbon disulphide, and separates in large, transparent, rhombic prisms; it crystallises from alcohol in prismatic needles and melts at  $162^\circ$ . Dibromocoumarilic acid,  $\text{C}_6\text{H}_2\text{Br}_2 \cdot \begin{smallmatrix} \text{CH} \\ \diagdown \quad \diagup \\ \text{O} - \text{CO} \end{smallmatrix} \cdot \text{C} \cdot \text{CO}_2\text{H}$ ,

prepared by hydrolysing the dibromide with alcoholic potash, melts at  $276^\circ$ , and is identical with that already obtained from tribromocoumarin (this vol., i, 421); the tribromocoumarin is therefore a

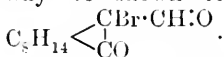
3 : 6 : 8-compound. *Tribromocoumarone*,  $C_6H_2Br_2 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} CBr$ , prepared by boiling the dibromide with sodium ethoxide for a short time, crystallises from alcohol in long, silky needles, and melts at  $119^\circ$ ; it is not altered by heating with alcoholic ammonia at  $160^\circ$  for several hours.

Perkin's  $\alpha$ -dibromocoumarin is shown to be a 3 : 6-compound, whilst the  $\beta$ -dibromocoumarin is the 6 : 8-derivative. *5-Bromocoumarone*,  $C_6H_3Br \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} CH$ , prepared by distilling bromocoumarilic acid with chalk, is a colourless oil, which solidifies in a freezing mixture and melts at  $8^\circ$ . The *dibromide* crystallises from absolute alcohol and melts at  $95^\circ$ . On boiling with sodium ethoxide for a short time, the dibromide is converted into 2 : 5-*dibromocoumarone*,



which crystallises in long needles and melts at  $78.5^\circ$ . T. M. L.

**Tautomeric Changes in Solution.** By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1900, **34**, 31—61).—The author has studied the changes of refraction and dispersion shown by solutions of tautomeric compounds, and thus endeavoured to establish the relative stability of the enolic and ketonic forms. The molecular refraction of oxymethylenecamphor (Claisen, *Abstr.*, 1895, i, 62), determined in two such different solvents as chloroform and methyl alcohol, undergoes no change, so that the enolic form is the stable one; there is no tendency for it to pass into the ketonic form, for this transformation would betray itself in a decrease of the molecular refraction. On the other hand, the bromine derivative of oxymethylenecamphor, prepared by Aschan and Brühl (*Abstr.*, 1894, i, 613), can in the same way be shown to exist as the stable ketonic form, namely,



A similar investigation of the  $\alpha$ - and  $\beta$ -modifications of ethyl formylphenylacetate (Wislicenus, *Abstr.*, 1895, i, 366) shows that the liquid  $\alpha$ -form is enolic, namely,  $OH \cdot CH : CPh \cdot CO_2Et$ ; this, however, is rapidly transformed by alcoholic solvents into the ketonic form  $CHO \cdot CHPh \cdot CO_2Et$ . The optical behaviour of its solutions in such solvents as chloroform and benzene, which are weak in energy (compare *Abstr.*, 1899, ii, 735), shows that the solid  $\beta$ -modification is isomeric with the  $\alpha$ -modification and equally saturated (possessing also an ethylene linking); it therefore differs from the ketonic form above referred to. Whether the differences between the  $\alpha$ - and  $\beta$ -modifications depend on stereoisomerism, position isomerism, or unequal degree of association, cannot be determined. The alcoholic solvents, being richer in energy than chloroform or benzene, convert the solid  $\beta$ -ester, as quickly as the  $\alpha$ -ester, into the liquid ketonic form.

J. C. P.

**Synthesis of  $\beta$ -Benzoyl- $\alpha$ -methylpropionic (Phenylmethylbutanonic) Acid.** By TIMOTHÉE KLOPP (*Bull. Soc. Chim.*, 1900, [iii], **23**, 511—512).—Pyrotartaric anhydride reacts with benzene in

the presence of aluminium chloride to form  $\beta$ -benzoyl- $\alpha$ -methylpropionic acid,  $\text{CH}_3\text{Bz}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , which crystallises in white needles melting at  $135\text{--}136^\circ$ , and is identical with the acid obtained by the action of potassium hydroxide on methyl phenacylmethylecyanoacetate (Abstr., 1898, i, 586).

N. L.

*p*-Toluoyl-*o*-benzoic Acid. By HEINRICH LIMPRICHT and OTTO WIEGAND (*Annalen*, 1900, 311, 178—193. Compare Abstr., 1898, i, 322).— $\beta$ -Methylantraquinone,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\text{C}_6\text{H}_3\text{Me}$ , prepared by

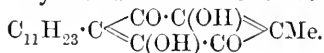
heating a solution of *p*-toluoyl-*o*-benzoic acid in concentrated sulphuric acid, crystallises from alcohol in white needles and melts at  $175\text{--}176^\circ$ ; the crystals are usually yellowish, however. When heated with zinc dust, the corresponding hydrocarbon,  $\beta$ -methylanthracene, is produced; it is also formed when  $\beta$ -methylantraquinone is heated with zinc dust and ammonia, and crystallises from alcohol in small white scales melting at  $207^\circ$ .

Distillation converts *p*-toluoyl-*o*-benzoic acid into substances resulting from elimination of water. At least two compounds are produced, melting at  $205\text{--}212^\circ$  and  $305\text{--}310^\circ$ , for which the authors suggest the formulæ  $\text{C}_{30}\text{H}_{22}\text{O}_5$  and  $\text{C}_{60}\text{H}_{60}\text{O}_{13}$  respectively; when these are heated with alcoholic potash, *p*-toluoyl-*o*-benzoic acid is regenerated, whilst oxidation with alkaline permanganate gives rise to benzophenonedicarboxylic acid.

The compound,  $\text{C}_{60}\text{H}_{42}\text{O}_9$ , prepared by heating *p*-toluoyl-*o*-benzoic acid above  $260^\circ$ , or the chloride at  $190^\circ$ , is a red powder melting at  $160\text{--}165^\circ$ ; the compound,  $\text{C}_{45}\text{H}_{30}\text{O}_6$ , which is also formed, is a red powder, and melts at  $155^\circ$ .

M. O. F.

**Embelic Acid.** By ARTHUR HEFFTER and W. FEUERSTEIN (*Arch. Pharm.*, 1900, 238, 15—28. Compare Warden, *Pharm. J.*, 1888, [iii], 18, 601; 19, 305).—Orange-red embelic acid,  $\text{C}_{15}\text{H}_{28}\text{O}_4$ , melting at  $142^\circ$ , was prepared by extracting with ether the powdered berries of *Ribes embelia*, Burm. (*Myrsinaceae*); no other well-characterised constituent could be isolated. The acid dissolves in alkalis, and greyish-violet alkali salts are precipitated when excess of the alkali is added; with salts of the heavy metals coloured, flocculent precipitates are obtained; the dark brown *silver* salt has the composition  $\text{C}_{15}\text{H}_{26}\text{O}_4\text{Ag}_2$ . The acid condenses with amines, 1 mol. of water being eliminated; the products are hydrolysed by dilute acids; *anilinoembelic* and *o*-*toluidinoembelic* acids, which are reddish-violet, melt at  $185^\circ$  and  $130^\circ$ , the red *methylaminoembelic* acid melts at  $166.5^\circ$ . With benzoyl chloride in pyridine solution, a yellowish *dibenzoyl* derivative,  $\text{C}_{32}\text{H}_{36}\text{O}_6$ , melting at  $97\text{--}98^\circ$ , is formed. With zinc powder and hydrochloric acid, reduction to *hydroembelic* acid,  $\text{C}_{15}\text{H}_{30}\text{O}_4$ , takes place; this acid is colourless, melts at  $116\text{--}117^\circ$ , and oxidises readily to embelic acid. By permanganate in the cold embelic acid is oxidised to lauric acid,  $\text{C}_{11}\text{H}_{23}\cdot\text{CO}_2\text{H}$ , and formic acid; there were obtained in addition oily acids, not volatile with steam, and forming salts that, unlike those of lauric acid, are not decomposed by carbon dioxide. From these reactions, the conclusion may be drawn that embelic acid has some such constitution as



C. F. B.



**Thermochemistry of Gallic Acid.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1900, [iii], 23, 614—615).—The heat of dissolution of anhydrous gallic acid is  $-4.48$  Cal. Sodium gallate crystallises from water with  $3\text{H}_2\text{O}$ , the hydrated salt having a heat of dissolution  $-8.40$  Cal., that of the anhydrous salt being  $1.01$ . Combining these values with those obtained by Berthelot (*Abstr.*, 1885, 1177) for neutralisation of gallic acid by sodium hydroxide,  $\text{C}_7\text{H}_5\text{O}_5$  (sol.) +  $\text{NaOH}$  (sol.) =  $\text{C}_7\text{H}_5\text{O}_5\text{Na}$  (sol.) +  $\text{H}_2\text{O}$  (sol.) +  $20.86$  Cal.

W. A. D.

**Thermochemistry of 2:3:4-Trihydroxybenzoic Acid.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1900, [iii], 23, 616—617).—The heat of dissolution of anhydrous 2:3:4-trihydroxybenzoic acid is  $-6.3$  Cal.; the heats of neutralisation of the acid by successive mols. of sodium hydroxide are  $1\text{NaOH}$ ,  $13.04$  Cal.;  $2\text{NaOH}$ ,  $6.56$  Cal.;  $3\text{NaOH}$ ,  $2.18$  Cal.;  $4\text{NaOH}$ ,  $0.96$  Cal.;  $5\text{NaOH}$ ,  $0.91$  Cal., the total heat of neutralisation being  $23.65$  Cal. Although the acid contains 3 hydroxyls, the thermal values are only well defined for two of these, as in the case of gallic acid (Berthelot, *Abstr.*, 1885, 1177).

To isolate the *sodium* salt of the acid, its solution must be evaporated in a vacuum at the ordinary temperature, owing to its proneness to oxidation; it crystallises with  $3\text{H}_2\text{O}$ , the heat of dissolution being  $-6.89$  Cal., that of the anhydrous salt being  $-1.36$  Cal. The heat of formation of the salt  $\text{C}_7\text{H}_5\text{O}_5$  (sol.) +  $\text{NaOH}$  (sol.) =  $\text{C}_7\text{H}_5\text{O}_5\text{Na}$  (sol.) +  $\text{H}_2\text{O}$  (sol.) +  $19.62$  Cal., being slightly less than that of gallic acid (preceding abstract).

W. A. D.

**Synthesis of Phthalidetricarboxylic Acid and Phthalidedicarboxylic Acid:** a new Passage from the Aliphatic to the Aromatic Series. By OSCAR DOEBNER (*Annalen*, 1900, 311, 132—146).—The author has shown that when an aldehyde is heated with pyruvic acid and barium hydroxide, the corresponding alkylisophthalic acid is produced (*Abstr.*, 1891, 24). On subjecting glyoxylic acid to the same treatment, however, no definite product could be obtained, but a successful result was achieved by using a solution of potassium diacetoxyacetate (compare this vol., i, 473).

*Phthalidetricarboxylic acid*,  $\text{CO}_2\text{H} \cdot \text{CH} \cdot \underset{\text{CO-O}}{\text{C}} \cdot \text{H}_2(\text{CO}_2\text{H})_2$ , prepared by

heating potassium diacetoxyacetate with pyruvic acid and potassium or sodium hydroxide, crystallises from water in colourless needles and melts at  $270-280^\circ$ , after gradually losing carbon dioxide above  $200^\circ$ .

*Phthalidedicarboxylic acid*,  $\text{O} \left\langle \begin{smallmatrix} \text{H}_2 \\ \text{CO} \end{smallmatrix} \right\rangle \text{C}_6\text{H}_2(\text{CO}_2\text{H})_2$ , obtained on boiling an aqueous solution of the foregoing substance, crystallises from water in aggregates of colourless leaflets containing  $2\text{H}_2\text{O}$ , and melts at  $286^\circ$ , the water of crystallisation being driven off at  $140^\circ$ ; the *barium* salt contains  $4\text{H}_2\text{O}$ , the *strontium* salt  $8\text{H}_2\text{O}$ , and the *calcium* salt  $6\text{H}_2\text{O}$ , the *silver* salt being anhydrous. The *diethyl* ester crystallises from dilute alcohol in long needles, and melts at  $112^\circ$ ; the *dianilide* forms large, colourless plates, and melts above  $300^\circ$ .

Toluene is obtained by heating a mixture of barium phthalididicarboxylate with barium oxide, but the result of fusing the acid with potassium hydroxide is *methylbenzenetricarboxylic acid*,  $C_6H_2Me(CO_2H)_3$ , which crystallises from hot water in long needles melting at about  $315^\circ$ . 1:2:3:4-Benzenetetracarboxylic (prehnitic) acid is produced when phthalididicarboxylic acid is oxidised with potassium permanganate. M. O. F.

**Oxidation of Benzaldoxime.** By EUGEN BAMBERGER (*Ber.*, 1900, 33, 1781—1788).—Benzaldoxime, when oxidised by means of Caro's reagent, yields a mixture of benzaldehyde, benzoic acid, dibenzoylazoxime, benzamide (trace), nitrous acid, benzhydroxamic acid, and *isophenyl*-nitromethane (isolated as phenylnitromethane). The formation of the two last substances is especially noteworthy; the conversion of an oxime into a hydroxamic acid is analogous to the oxidation of an aldehyde to a carboxylic acid, whilst the transformation of benzaldoxime into *isophenyl*nitromethane, which recalls the oxidation of tertiary bases to amine oxides, resembles the formation of true nitro-compounds by the oxidation of true nitroso-derivatives.

The author explains the transformation observed by Scholl (*Abstr.*, 1888, 443) of oximes into the corresponding pseudonitroles under the action of nitrogen tetroxide, by assuming that, in the first instance, the latter oxidises the oxime to the corresponding *isonitro*paraffin. Thus acetoxime would initially yield secondary *isonitro*propane and nitrous acid, these two substances then interacting normally to form the pseudonitrole. V. Meyer's view (*Abstr.*, 1888, 702), based on Scholl's work, that the pseudonitroles may be regarded as the nitrites,  $R_2C:N \cdot O \cdot NO_2$ , of the oximes, does not therefore appear to be justified; moreover, the formation of pseudonitroles by the electrolytic oxidation of ketoximes (Schmidt, this vol., i, 332) also militates against this view.

It is stated in conclusion, without experimental data being given, that substituted benzaldoximes and also acetaldoxime yield the corresponding hydroxamic acids when treated with Caro's reagent; acetaldoxime yields in addition *isonitro*ethane. Since benzylamine yields benzaldoxime when treated with Caro's reagent (this vol., i, 281), benzhydroxamic acid and *isophenyl*nitromethane are amongst the products of the oxidation of benzylamine by this method.

W. A. D.

**Oxidations in Presence of Acetic Anhydride and Sulphuric Acid.** By JOHANNES THIELE and ERNST WINTER (*Annalen*, 1900, 311, 353—362).—A mixture of acetic anhydride and concentrated sulphuric acid is capable of oxidising methyl derivatives of benzene to the corresponding aldehydes, which are at once converted into the diacetyl derivatives.

*p*-Nitrobenzaldehyde diacetate,  $NO_2 \cdot C_6H_4 \cdot CH(OAc)_2$ , prepared from *p*-nitrotoluene and acetic anhydride with sulphuric, acetic, and chromic acids, crystallises from alcohol in white prisms and melts at  $125^\circ$ ; *o*-nitrobenzaldehyde diacetate melts at  $87-88^\circ$ .

*p*-Hydroxybenzaldehyde triacetate,  $OAc \cdot C_6H_4 \cdot CH(OAc)_2$ , obtained from

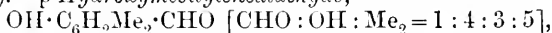
the acetyl derivative of *p*-cresol, crystallises from petroleum in prisms and melts at 93—94°.

*Trihydroxybenzaldehyde pentacetate*,  $(\text{OAc})_3 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{OAc})_2$ , produced when the triacetyl derivative of trihydroxytoluene is treated in the manner described, crystallises from alcohol in white needles melting at 130°.

*Terephthalaldehyde tetracetate*,  $\text{C}_6\text{H}_4[\text{CH}(\text{OAc})_2]_2$ , prepared from *p*-xylene, crystallises from alcohol in white leaflets melting at 164°. *isoPhthalaldehyde tetracetate* melts at 101°, and *phthalaldehyde tetracetate* at 132—133°.

Phthalaldehyde, prepared by hydrolysing the tetracetate, melts at 55—56°, and the dioxime at 251°. M. O. F.

**Action of Ethyl Nitrite on Trisubstituted Phenols.** By JOHANNES THIELE and HEINRICH EICHWEDE (*Annalen*, 1900, 311, 363—379).—*p*-Hydroxymesitylenealdehyde,



prepared from mesitol by the action of a concentrated solution of ethyl nitrite in alcohol, crystallises from benzene in colourless, nacreous leaflets, and melts at 113·5—114°; the *triacetate* melts at 95°, and the *benzoyl* derivative at 105°. The *phenylhydrazone* is a crystalline powder melting at 143°, and the *phenylhydrazone* of the benzoyl derivative crystallises from alcohol in colourless needles melting at 184°. The *oxime* melts at 169·5°, and yields the *hydrochloride* as a white, crystalline powder which melts and decomposes at 157°; the *diacetyl* derivative of the oxime crystallises from carbon disulphide, and melts at 113°.

*p*-Hydroxymesitylenonitrile,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CN}$ , crystallises from petroleum in lustrous needles melting at 126°; the *acetyl* derivative, obtained when the foregoing oxime is treated with boiling acetic anhydride, forms slender, white needles melting at 98°.

*p*-Hydroxymesityleneimino-ether,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_3 \cdot \text{C}(\text{OEt})\text{:NH}$ , crystallises from benzene and melts at 144°, when it decomposes; the *hydrochloride*, obtained by passing hydrogen chloride into a boiling alcoholic solution of *p*-hydroxymesitylenonitrile, is a white powder sparingly soluble in water.

4:6-Dibromo-2-nitrophenol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH}$ , produced when tribromophenol is treated with a concentrated solution of ethyl nitrite in absolute alcohol, melts at 117·5°; the corresponding 4:6-dibromo-2-aminophenol melts at 99° (Hölz gives 91—92°).

*Bromonitrocresol*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$  [ $\text{Me} : \text{NO}_2 : \text{OH} : \text{Br} = 1 : 3 : 4 : 5$ ], prepared from dibromo-*p*-cresol by the action of ethyl nitrite in alcohol, crystallises from alcohol in lustrous, yellow needles and melts at 69°; it is also produced by brominating *o*-nitro-*p*-cresol. *Bromoaminocresol*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$  [ $\text{Me} : \text{NH}_2 : \text{OH} : \text{Br} = 1 : 3 : 4 : 5$ ], obtained by reducing the foregoing substance with stannous chloride and hydrochloric acid, crystallises from alcohol in colourless needles and melts at 93°; the *hydrochloride* forms thin, lustrous leaflets and blackens at 240—250°.

*Bromonitrocresol*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$  [ $\text{Me} : \text{OH} : \text{NO}_2 : \text{Br} = 1 : 2 : 3 : 5$ ],

prepared from dibromo-*o*-cresol and ethyl nitrite, melts at  $88^{\circ}$ , being identical with the substance described by Claus and Jackson.

*p*-Bromo- $\beta$ -cresotic acid,

$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$  [ $\text{Me} : \text{OH} : \text{CO}_2\text{H} : \text{Br} = 1 : 2 : 3 : 5$ ],

produced on adding bromine to a solution of  $\beta$ -cresotic acid in glacial acetic acid, crystallises from ethyl acetate in white needles, and melts at  $231$ – $232^{\circ}$ , when it decomposes; the *methyl* and *ethyl* esters melt at  $109^{\circ}$  and  $75^{\circ}$  respectively. The action of ethyl nitrite is very slow, the product consisting of nitrobromocresol melting at  $88^{\circ}$ .

M. O. F.

**2-Methylchromone.** By M. BLOCH and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 1998–1999. Compare this vol., i, 308).—2-Methoxyacetylacetophenone,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2\text{Ac}$ , obtained when a mixture of methyl methoxysalicylate, acetone, and sodium is left for 12 hours, crystallises in long, broad, striated prisms melting at  $36$ – $37^{\circ}$ , and in alcoholic solution gives a red coloration with ferric chloride. By the action of hydriodic acid it is converted into 2-methyl-

chromone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} - \text{CMe} \\ | \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ , which crystallises in clusters of white needles melting at  $70$ – $71^{\circ}$ , and, when dissolved in sulphuric acid, exhibits a violet-blue fluorescence.

R. H. P.

**The Friedel-Crafts Reaction.** By H. KRONBERG (*J. pr. Chem.*, 1900, [ii], 61, 494–496).—The additive compound of benzoyl chloride with aluminium chloride is regarded as having the constitution  $\text{C}_6\text{H}_5 \cdot \text{CCl}_2 \cdot \text{O} \cdot \text{AlCl}_2$ ; this reacts with benzene to form the additive compound of benzophenone and aluminium chloride, which is formulated as  $\text{CPh}_2\text{Cl} \cdot \text{O} \cdot \text{AlCl}_2$ , and is decomposed by water into benzophenone and aluminium oxychloride.

T. M. L.

**New Derivative of Benzophenone.** By WILLIAM OECHSNER DE CONINCK and DERRIEN (*Compt. rend.*, 1900, 130, 1768–1770).—A solution of benzophenone in concentrated formic acid, when exposed to diffused light, develops a light yellow coloration which gradually deepens in tint; browner shades are produced when the solution is placed in direct sunlight. Benzophenone, which is but slightly soluble in dilute acetic acid, gradually dissolves in this medium under the influence of the solar radiation, the solution thus produced slowly developing a brown coloration.

Benzophenone, when exposed to the indigo and violet parts of the spectrum, soon melts and remains liquid, but the phenomenon is not due to allotropic change, for after solidification the substance is found to have its original melting point.

A solution of benzophenone in 95 per cent. alcohol, when exposed to direct sunlight, slowly develops a pale yellow coloration and deposits colourless, birefractive crystals melting at  $182^{\circ}$ , an appreciable quantity of aldehyde being simultaneously produced. The compound, which has the empirical formula  $\text{C}_{17}\text{H}_{16}\text{O}$ , is probably produced by the interaction of equal mols. of benzophenone, aldehyde, and alcohol, and may have the constitution  $\text{CPh}_2 \cdot \text{CH} \cdot \text{CEtO}$ . A compound

melting at  $180^{\circ}$  is produced in a similar manner with a solution of benzophenone in methyl alcohol, whilst an alcoholic solution of acetophenone yields a substance melting at  $120^{\circ}$ . G. T. M.

**Derivatives of *p*-Aminobenzophenone.** By PAUL DINGLINGER (*Annalen*, 1900, 311, 147—153).—The *phenylhydrazone* of *p*-aminobenzophenone,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} : \text{N} \cdot \text{NHPh}$ , prepared by heating an alcoholic solution of *p*-aminobenzophenone with excess of phenylhydrazine, crystallises in lustrous yellow needles and melts at  $169^{\circ}$ .

*p*-Benzophenylsuccinimide,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$ , obtained by fusing a mixture of succinic anhydride with *p*-benzoaniline (*p*-aminobenzophenone), crystallises from hot alcohol in small, dull-yellow prisms and melts at  $175^{\circ}$ .

*Ethyl p*-benzophenyloxamate,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , produced when *p*-benzoaniline is heated with ethyl oxalate (1 mol.), crystallises from alcohol in white leaflets and melts at  $112^{\circ}$ .

*p*-Benzophenylmethylurethane,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Me}$ , obtained from *p*-benzoaniline and methyl chlorocarbonate, forms white, lustrous leaflets and melts at  $155^{\circ}$ . Fusion, followed by distillation, converts this compound into methyl alcohol and *benzophenylcarbimide*,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CO}$ , a yellow, granular powder which begins to melt at  $201^{\circ}$ .

*Dibenzophenylcarbamide*,  $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COPh})_2$ , prepared by heating benzophenylcarbimide with benzoaniline dissolved in benzene in a reflux apparatus, crystallises in small, yellow needles melting at  $189^{\circ}$ ; it is more readily produced by passing phosgene into a solution of benzoaniline in boiling benzene.

*p*-Benzophenylthiocarbimide,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CS}$ , obtained by distilling dibenzophenylthiocarbamide with phosphoric acid, crystallises from benzene and melts at  $122^{\circ}$ .

*p*-Benzophenylthiocarbamide,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$ , prepared by the action of ammonia on the foregoing substance, crystallises in lustrous, white leaflets and melts at  $198^{\circ}$ .

The *p*-benzoanilide of *p*-benzoanilinocinnamonylformic acid,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{CH} : \text{CHPh}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COPh}$ , produced on heating alcoholic *p*-benzoaniline with pyruvic acid and benzaldehyde, crystallises from glacial acetic acid in slender, white needles and melts at  $186^{\circ}$ .

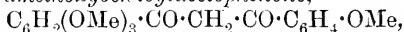
When *p*-aminobenzophenone is fused with zinc chloride, benzoic acid and benzanilide are formed. M. O. F.

**Action of Ethyl Mercaptan on some Diatomic Ketones.** By B. LLAGUET (*Bull. Soc. Chim.*, 1900, [iii], 23, 507—509).—Ethyl mercaptan reacts with benzoin in the presence of hydrochloric acid or zinc chloride to form a compound,  $\text{CPh}(\text{SEt})_2 \cdot \text{CHPh} \cdot \text{OH}$ , which crystallises from dilute alcohol in white needles melting at  $93$ — $94^{\circ}$ , and is oxidised to benzil by potassium permanganate or nitric acid. Benzil, when similarly treated, yields a compound,  $\text{CPh}(\text{SEt})_2 \cdot \text{COPh}$ , which crystallises from alcohol in white, prismatic needles, and from acetic acid in octahedra melting at  $73$ — $74^{\circ}$ ; oxidation reconverts it into

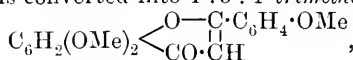
benzil. With acetyl acetone, ethyl mercaptan forms a yellow, oily liquid of the composition  $\text{CMe}(\text{SEt})_2 \cdot \text{CH}_2\text{Ac}$ , which has a sp. gr. 2.008 at  $13.5^\circ$ , and boils at  $180\text{--}185^\circ$  under 240 mm. and at  $179\text{--}183^\circ$  under 215 mm. pressure. When treated with sodium ethoxide in alcoholic solution, it yields a *sodium* derivative crystallising in white needles, whilst with sodium hydrogen sulphite it forms a *compound* which also crystallises in needles. No definite compounds could be isolated from its oxidation products. N. L.

**Synthesis of 1:3:4'-Trihydroxyflavone (Apigenin).** By J. CZAJKOWSKI, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1900, 33, 1988—1997).—Assuming from the researches of A. G. Perkin (*Trans.*, 1897, 71, 805) that apigenin is 1:3:4'-trihydroxyflavone, the authors have synthesised this compound, and found that pure apigenin is identical with it, but that the apigenin which Perkin used was not pure.

2:4:6:4'-*Tetramethoxybenzoylacetophenone*,



obtained by heating 2:4:6-trimethoxyacetophenone and ethyl anisate with sodium in xylene solution at  $120^\circ$  for 12 hours, crystallises in colourless plates or needles which melt at  $91^\circ$ . When treated with hydriodic acid, it is converted into 1:3:4'-*trimethoxyflavone*,



which crystallises in rosettes of long, white needles melting at  $156^\circ$ , and when further treated with hydriodic acid yields 1:3:4'-*trihydroxyflavone*, which crystallises in small, yellowish-white leaflets melting at  $347^\circ$ , and does not dye mordanted cotton; this proves to be identical with apigenin obtained by the purification (by means of hydriodic acid) of the crude product yielded by the hydrolysis of apiin.

1:3:4'-*Triacetoxyflavone* (triacetylapiogenin) crystallises in silky, white needles which melt at  $181\text{--}182^\circ$ ; 3:4'-dimethoxy-1-hydroxyflavone crystallises in yellowish needles which melt at  $170\text{--}171^\circ$ , and yields an acetyl derivative melting at  $193\text{--}194^\circ$ ; the corresponding diethoxy-derivatives melt at  $163\text{--}164^\circ$  and  $148\text{--}149.5^\circ$  respectively (compare Perkin, *loc. cit.*). R. H. P.

**Oxidation of the Oximes of Unsaturated Compounds.** By CARL D. HARRIES (*Ber.*, 1900, 33, 1999—2001. Compare Abstr., 1899, i, 566).— $\alpha$ -Mesityloxime or mesitylnitrimine, when treated with dilute nitric acid, yields a *compound*,  $\text{C}_6\text{H}_5\text{O}_4\text{N}_3$ , which forms golden-yellow crystals melting at  $127\text{--}128^\circ$ , and reacts with aniline, forming a crystalline *compound* which melts at  $86\text{--}88^\circ$ .

Benzylideneacetoxime, when treated with acetic acid and amyl nitrite, yields an insoluble *compound*,  $\text{C}_{10}\text{H}_9\text{O}_3\text{N}_3$ , which melts at  $210^\circ$ , and, when treated with dilute nitric acid, an easily soluble *compound* melting at  $159^\circ$ . R. H. P.

**Action of Acetic Anhydride and Sulphuric Acid on Quinones.** By JOHANNES THIELE and ERNST WINTER (*Annalen*, 1900, 311, 341—352. Compare Abstr., 1898, i, 469).—The *diacetyl*

derivative of chloroquinol,  $C_{10}H_9O_4Cl$ , obtained from quinone by the action of zinc chloride dissolved in acetic anhydride, crystallises from methyl alcohol in rhombic plates, and melts at  $71-72^\circ$ .

The *triacetyl* derivatives of 1:2:4-trihydroxynaphthalene, prepared alike from  $\alpha$ - and  $\beta$ -naphthaquinones by the action of acetic anhydride mixed with concentrated sulphuric acid or zinc chloride, crystallises from alcohol in groups of needles, and melts at  $134-135^\circ$ ; alcoholic hydrochloric acid hydrolyses it to 1:2:4-trihydroxynaphthalene, which crystallises from a large quantity of benzene in almost colourless needles melting at  $154^\circ$ . Alcoholic solutions of trihydroxynaphthalene darken on exposure to air, and after a long interval deposit deep red crystals of hydroxynaphthaquinone, which melt at  $186-188^\circ$  and decompose at  $190^\circ$ ; the *acetyl* derivative, obtained by treatment with boiling acetic anhydride, and also by the action of acetic anhydride mixed with concentrated sulphuric acid, crystallises from alcohol in yellow leaflets and melts at  $130^\circ$ .

The diacetyl derivative of naphthazarine (dihydroxy- $\beta$ -naphthaquinone) is readily obtained by treating naphthazarine with a solution of zinc chloride in acetic anhydride, or a mixture of the latter substance with concentrated sulphuric acid. The *pentacetyl* derivative of pentahydroxynaphthalene,  $C_{20}H_{18}O_{10}$ , produced by the further action of acetic anhydride mixed with concentrated sulphuric acid, separates from alcohol as a white, crystalline powder melting at  $179^\circ$ .

*Trihydroxynaphthaquinone*,  $C_{10}H_6O_5$ , prepared by hydrolysing the foregoing pentacetyl derivative with alcoholic sulphuric acid, rendering the dark liquid faintly alkaline with sodium carbonate, and then acidifying with sulphuric acid, separates from xylene as a red, crystalline powder which melts at  $195^\circ$ .

The *triacetyl* derivative of trihydroxytoluene, prepared by the action of acetic anhydride mixed with concentrated sulphuric acid on toluquinone, crystallises from alcohol and melts at  $114-115^\circ$ ; hydrolysis converts it into 2:4:5-trihydroxytoluene, which melts at  $131-132^\circ$ .

*p-Hydroxytoluquinone*,  $C_7H_6O_3$ , produced on oxidising trihydroxytoluene with ferric chloride, crystallises from xylene in lustrous, yellow leaflets which melt and decompose at  $142^\circ$ ; the *acetyl* derivative separates from petroleum in slender, yellow prisms and melts at  $75-76^\circ$ .

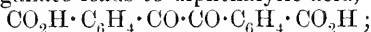
The *tetracetyl* derivative of tetrahydroxytoluene, prepared by the action of acetic anhydride mixed with concentrated sulphuric acid on hydroxytoluquinone, separates from methyl alcohol as a white, crystalline powder melting at  $132-133^\circ$ ; *tetrahydroxytoluene*  $[Me:(OH)_4 = 1:2:3:4:5 \text{ or } 1:2:4:5:6]$  separates as a crystalline powder from toluene and melts at  $170-171^\circ$ .

M. O. F.

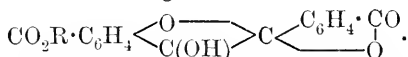
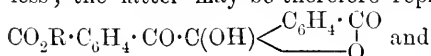
**Oxidation Products of Chrysene.** By CARL GRAEBE and F. HONIGSBERGER (*Annalen*, 1900, 311, 257-275. Compare Abstr., 1896, i, 443).—Chrysoquinone was first obtained by Liebermann on oxidising the hydrocarbon with chromic acid in acetic acid, but it is found more convenient to substitute sodium dichromate for chromic acid as only one-fourth the quantity of acetic acid is then required. The quinone melts at  $235^\circ$  ( $239.5^\circ$  corr.). When the blue solution

in concentrated sulphuric acid is largely diluted, the liquid exhibits a characteristic absorption spectrum having a broad, dark band,  $\lambda$  610—540; concentrated solutions cut off the orange, the yellow, and a portion of the green of the spectrum.

Further oxidation of chrysoquinone with a boiling dilute solution of potassium permanganate leads to diphthalic acid,



the *calcium* salt contains  $\frac{1}{2}\text{H}_2\text{O}$ , which is removed at  $150^\circ$ , and the *potassium* salt is anhydrous. Both salts are yellow, and the dimethyl ester is yellow, the monomethyl and monoethyl esters being colourless; the latter may be therefore represented by one of the formulæ



Diphthalic acid, unlike benzilmonocarboxylic acid, occurs in one modification only, and this is colourless; it is best represented, therefore,

by the tautomeric formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{---} \text{C}(\text{OH}) \cdot \text{C}(\text{OH}) \text{---} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \quad \text{O} \cdot \text{CO} \end{array} \text{C}_6\text{H}_4$ , support

being given to this expression by the fact that acetyl chloride converts the substance into the *diacetyl* derivative, which crystallises from glacial acetic acid in colourless needles and melts at  $234^\circ$ . Diphthalic acid is also produced by the oxidation of chrysoketone with potassium permanganate.

Chrysenic acid,  $\text{C}_{10}\text{H}_7 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , obtained by Bamberger and Burgdorf from the action of fused caustic potash on chrysoquinone and chrysoketone, is more conveniently prepared by adding a mixture of chrysoquinone and lead peroxide to the fused alkali; it melts at  $187\text{—}189^\circ$  ( $190^\circ$  corr.). The *amide* melts at  $169.5^\circ$ .

2'-Amino-2-phenylnaphthalene,  $\text{C}_{10}\text{H}_7 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , prepared by the action of sodium hypobromite on the amide of chrysenic acid, crystallises from dilute alcohol in needles and melts at  $95^\circ$ ; the *hydrochloride* melts at  $205^\circ$ .

*Chrysoquinoneoxime*,  $\text{C}_{16}\text{H}_{10} \begin{array}{c} \text{C:NOH} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ , obtained by heating the

quinone with alcoholic hydroxylamine (1 mol.), crystallises from glacial acetic acid and melts at  $160\text{—}161^\circ$ ; the solution in concentrated sulphuric acid is reddish-violet, and boiling dilute caustic soda dissolves it also, forming a yellowish-brown liquid, which, on cooling, deposits bronze-coloured needles of the *sodium* derivative.

According to the conditions under which the change is effected, the Beckmann transformation of chrysoquinoneoxime gives rise to two amic acids. The action of glacial acetic acid, saturated with hydrogen chloride, converts chrysoquinoneoxime at  $100^\circ$  into the *amic acid*,  $\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}$ , which melts at  $220^\circ$ , and the *isomeride* melting at  $260^\circ$ , of which the former preponderates; if the transformation is carried out at  $130\text{—}140^\circ$ , the latter substance is produced, along with *chrysoketone*-

*carboxylic acid*,  $\text{C}_{10}\text{H}_5(\text{CO}_2\text{H}) \begin{array}{c} \text{---} \text{CO} \text{---} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array}$  or  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{---} \text{CO} \text{---} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \end{array}$ , which melts at  $283^\circ$ , and yields chrysoketone when distilled with lime. M. O. F.



**Influence of the Amount of Water on the Specific Rotation of Alcoholic Solutions of Camphor.** Valuation of Spirit of Camphor. By ALFRED PARTHEIL and A. VAN HAAREN (*Arch. Pharm.*, 1900, 238, 164—166).—It is shown that the percentage of camphor dissolved in aqueous alcohol is very approximately given by  $1.5152a$ , where  $a$  is the rotation produced in a 200 mm. tube; the sp. gr. of the alcohol used has little influence on the result. For finding the sp. gr. of the alcohol used in preparing a sample of spirit of camphor, the expression  $100 - p \frac{100}{d} - 1.05 p$  gives good results,  $p$  denoting the percentage of camphor present, and  $d$  the sp. gr. of the camphor spirit.

W. A. D.

**Decomposition Products of Campherimine.** By FRIEDRICH MAHLA and FERDINAND TIEMANN (*Ber.*, 1900, 33, 1929—1939. Compare Abstr., 1896, i, 85).—When campherimine is heated on the water-bath in a reflux apparatus attached to wash-bottles containing alcohol, and air is slowly bubbled through the hot liquid for 8—10 hours, the products are camphor, dihydrocampholenitrile, the corresponding amide, and the nitrile of isopropylheptanonic acid.

*Dihydrocampholenitrile*,  $\text{CN} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$ , is readily volatile in steam and forms a colourless liquid boiling at  $225\text{--}228^\circ$ ; it has a sp. gr. 0.90904, refractive index 1.46108, molecular refraction 45.60, and its rotation in a 10 cm. tube is  $+28^\circ 53'$ . The corresponding *amide*, readily obtained by the partial hydrolysis of the nitrile with alcoholic potassium hydroxide, crystallises from ethyl acetate in plates melting at  $143^\circ$  and is readily soluble in most organic solvents with the exception of light petroleum; it is dextrorotatory and when boiled for some time with alcoholic potash yields *dihydrocampholenic acid*,  $\text{C}_{10}\text{H}_{15}\text{O}_2$ , which is best purified by passing ammonia into the dry ethereal solution of the acid and decomposing the ammonium salt with mineral acid. It is a colourless oil, distils at  $160^\circ$  under 22 mm. or at  $258^\circ$  under atmospheric pressure, has a sp. gr. 0.98048, refractive index 1.46277, molecular refraction 47.73, and its rotation in a 10 cm. tube is  $+28^\circ 26'$ . It is readily volatile in steam, yields insoluble *calcium*, *silver*, *lead*, and *copper* salts, and does not combine with bromine, but readily decolorises dilute alkaline permanganate. Its *ethyl* ester distils at  $230^\circ$  and in a 10 cm. tube has a rotation  $+25^\circ 33'$ . The acid is probably identical with that described by Guerbet (Abstr., 1895, i, 61). When oxidised with alkaline permanganate, it yields an *acid*,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{CMe}_2 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , crystallising in rhombic plates melting at  $175^\circ$ , together with a small amount of an *acid*,  $\text{C}_{10}\text{H}_{11}\text{O}_6$ , which crystallises in rhombic prisms melting at  $198^\circ$ , and readily soluble in ether, alcohol, or water; the latter is also obtained when the hydroxy-acid,  $\text{C}_{10}\text{H}_{16}\text{O}_5$ , is further oxidised with permanganate, but if Beckmann's mixture is employed, *isocamphoronic acid* is formed; *isocamphoronic acid* is also obtained when hydrocampholenic acid is oxidised with nitric acid.

*5-isoPropylheptanone-2-nitrile-7*,  $\text{CN} \cdot \text{CH}_2 \cdot \text{CHPr}^{\delta} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ac}$ , ob-

tained by fractional distillation under reduced pressure from the products which are not volatile in steam, is an oil distilling at  $174\text{--}180^\circ$  under 32 mm. pressure or, after purification, by aid of its *semicarbazone* (which melts at  $135^\circ$ ), at  $157^\circ$  under 16 mm. pressure. It has a sp. gr. 0.9402 at  $23^\circ$ , a refractive index 1.45129, and a molecular refraction 47.83. When boiled with alcoholic potash for 3 hours, the greater part of the nitrile is transformed into an isomeric substance,  $\text{C}_{10}\text{H}_7\text{ON}$ , melting at  $127^\circ$ ; this yields a *semicarbazone* melting at  $214^\circ$ , has feebly basic properties, and yields a sparingly soluble *aurichloride*; when warmed with excess of mineral acids, an odour of carvone is developed, and an oil formed which yields a *semicarbazone* melting at  $154^\circ$ .

*iso*Propylglutaric acid is formed when the *isopropylheptanonenitrile* is oxidised with permanganate. J. J. S.

**Citral and its Isomeric Forms.** By PHILIPPE BARBIER (*Bull. Soc. Chim.*, 1900, [iii], 23, 617—618).—A claim for priority.

W. A. D.

**Syntheses in the Terpene Series.** By IWAN L. KONDAKOFF and IWAN SCHINDELMEISER (*J. pr. Chem.*, 1900, [ii], 61, 477—490).—Tables are given of the values recorded by previous workers and those obtained in the present research for the physical constants of 1-methyl-3-cyclohexanone, 1-methyl-3-cyclohexanol, 1-methyl-3-cyclohexanol bromide, and tetrahydrotoluene. In presence of zinc chloride, tetrahydrotoluene forms with acetyl chloride an additive compound which has an odour similar to that of carvone, and yields an oxime; with moist silver oxide, it is converted into a keto-alcohol. Additive compounds with acetic anhydride and acetic acid are also formed under similar conditions.

In the reduction of 1-methyl-3-cyclohexanone, a crystalline substance is produced which is not volatile with steam; when crystallised from water, it forms hydrated crystals melting at  $73^\circ$ , but when dried in a desiccator melts at  $93\text{--}94^\circ$ , or at  $92.5^\circ$  when crystallised from alcohol; a 10 per cent. solution has  $\alpha + 1^\circ 1'$  in a 1 dm. tube at  $20^\circ$ ; the substance appears to give two bromides, one liquid and the other a solid melting at  $126^\circ$ ; on treating the bromide with moist silver oxide, the product has a powerful odour of pelargonium oil. The substance is probably a pinacone, as has been suggested by Wallach (*Nachrichten K. Ges. Wiss. Göttingen*, 1897, 315). T. M. L.

**Action of Fuming Nitric Acid on Camphene.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 535—540).—When camphene is dissolved in chloroform and gradually added to well-cooled fuming nitric acid, it is converted into a mixture of two isomeric nitrates of the composition  $\text{C}_{10}\text{H}_{16}\text{HNO}_3$ , one of these being decomposed when distilled under diminished pressure, whilst the second is more stable, boils at  $110^\circ$  under 10 mm. pressure, has a sp. gr. 1.0988 at  $0^\circ$ , and is converted by treatment with alcoholic potash into camphene and potassium nitrate. Since the nitrates of secondary alcohols are very frequently converted by the action of potash into potassium *nitrite* and a ketone, it seems probable that the nitrate described is derived from a tertiary alcohol, and that camphene itself

has not the constitution  $C_5H_{14} \begin{smallmatrix} <CH \\ | \\ CH \end{smallmatrix}$ , but contains the complex  $>C:CH_2$  or  $\geq C \cdot CH_3$ . This result is shown to be in accordance with the author's views on the constitution of camphor and its derivatives.

N. L.

**Isoprene.** By WLADIMIR MOKIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 207—216. Compare Abstr., 1899, i, 726).—On oxidising isoprene dibromide with permanganate, the corresponding glycol (dibromohydrin) is obtained, and this by the action of zinc dust is converted into a hydrocarbon (*loc. cit.*), which the author now shows to be identical with isoprene. If isoprene has the open-chain formula,  $CH_2:CM e \cdot CH:CH_2$ , the hydrocarbon obtained by the reduction of the dibromohydrin would have the structure  $CM e \begin{smallmatrix} <CH_2 \\ | \\ CH \end{smallmatrix} > CH_2$ , whilst if the latter be taken as the formula of isoprene, its dibromohydrin should yield the open-chain compound  $CH_2:CM e \cdot CH:CH_2$ , the identity of the initial and end products being in either case due to isomeric change. By the action of an acetic acid solution of hydrogen bromide on isoprene, a bromide is obtained of the composition  $C_5H_9Br$ ; it boils at  $66-67^\circ$ , and has the sp. gr. 1.3075 at  $0^\circ/0^\circ$  and 1.2819 at  $20^\circ/0^\circ$ ; the same bromide is obtained from *as*-dimethylallene and hydrogen bromide. On treating this bromide with alcoholic potash, the corresponding alcohol,  $C_5H_{10}O$ , prepared by Kondakoff (*J. Russ. Phys. Chem. Soc.*, 1889, 61) is obtained; it boils at  $97-99^\circ$ , and has the sp. gr. 0.8417 at  $0^\circ/0^\circ$  and 0.8242 at  $20^\circ/0^\circ$ . [With NICOLAI A. MENSCHUTKIN.—The constant of esterification of this alcohol at  $100^\circ$  by acetic anhydride in presence of 15 volumes of benzene is 0.00025, the corresponding values for allyl and  $\alpha$ -methylallyl alcohols, methylallylcarbinol, and trimethylcarbinol being 0.02871, 0.02673, 0.00643, and 0.00091 respectively.] These numbers show that the alcohol from isoprene is tertiary, as also is the bromide from which it is prepared; and the open-chain formula for isoprene is the only one which can give rise to a tertiary bromide identical with that obtained from *as*-dimethylallene.

The statement of Ipatieff (Abstr., 1899, i, 657) that a primary bromide is obtained by the addition of hydrogen bromide to diethylallene is regarded by the author as erroneous.

T. H. P.

**Civet, Jasmine, and Oil of Roses.** By HEINRICH WALEAUM (*Ber.*, 1900, 23, 1903—1905).—Commercial civet, prepared from the African civet-cat, *Viverra civetta*, has a strongly faecal odour, and contains 0.1 per cent. of scatole, but no indole. As oil of jasmine, obtained from the pomade prepared by means of civet, contains indole (Hesse, Abstr., 1899, i, 48), although the oil extracted from the fresh jasmine blossoms does not contain this (Hesse, this vol., i, 454), it appears that the indole is developed in the blossoms after being plucked and during their treatment with the civet. Similarly, rose blossoms on keeping appear to elaborate phenylethyl alcohol, since the latter is present in marked quantity in the oil obtained from

dried rose leaves, although it is entirely absent from oil of roses prepared from fresh blossoms. W. A. D.

**Essential Oil of Jasmine.** By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 555—556).—The discrepancies between the results obtained by Verley (*Abstr.*, 1899, i, 376) and by Hesse and Müller (*Abstr.*, 1899, i, 377, 441) in the examination of essential oil of jasmine are attributed to the fact that the oil was extracted from jasmine pomade, in the preparation of which rose-water, oil of orange flowers, benzoin, and alum are sometimes used. The following results were obtained from samples of oil of jasmine prepared (1 and 2) from pomade without extraneous additions; (3) by direct distillation from the flowers; (4) by distillation of flowers from which a portion of the odoriferous substances had been previously extracted by the usual process (*enfleurage à froid*).

	1.	2.	3.	4.
Sp. gr. at 17.5°.....	0.9099	0.9201	0.9246	0.8900
Rotatory power per 100 mm. ....	+ 2°30'	+ 2°40'	+ 1°40'	+ 3°50'
Saponification number	103.6	126.0	155	77
Esters as linalyl acetate, per cent. ...	36.26	44.10	54.39	26.95
Esters as benzyl acetate, per cent. ...	27.70	33.75	41.65	20.62
				N. L.

**Empyreumatic Oil of Juniper.** By CATHELINEAU and JEAN HAUSER (*Bull. Soc. Chim.*, 1900, [iii], 23, 557—559. Compare *Abstr.*, 1899, i, 536, 711).—The dark brown resin, soluble in caustic soda, of which 19 grams were obtained, as previously described (*Abstr.*, 1899, i, 536), from 400 c.c. of empyreumatic oil of juniper, is separated by treatment with ether into a semi-liquid portion, of agreeable odour, which could not be identified, and an insoluble substance having the composition  $C_{12}H_{11}O_3$ , or some multiple of this. The latter, which has the properties of a feeble acid, is precipitated by acids from its solution in alkalis in the form of brown, amorphous flocks, but when the liquid is shaken with ether and warmed, these are converted into microscopic crystals. The acid is insoluble in water or ether, but more or less soluble in alcohol, chloroform, or concentrated acetic acid.

N. L.

**Essential Oil of Lavender and the Causes of the Variation in the amount of Esters contained in it.** By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 549—554).—A number of samples of oil of lavender from various sources were examined in order to ascertain the conditions influencing the proportion of esters, by which the commercial value of the oil is determined. The altitude of the place of growth appears not to affect the chemical composition and physical properties of the oil, although it may possibly have some influence on the delicacy of the perfume. The oil obtained from the flowers is incomparably superior in odour to that from the leaves and stalks, but no great differences in the chemical and physical characters

of the two are found. The conduct of the distillation is the most important factor in the production of an oil rich in esters. This operation should be carried out as quickly as possible, in order to avoid loss by partial hydrolysis, whilst at the same time it should be pushed to its utmost limit, since the proportion of esters in the various fractions increases continuously as the distillation progresses. The water used should contain but little dissolved solids. N. L.

**Essential Oils of Neroli and Petit Grain.** By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 605—608).—Charabot and Pillet's (Abstr., 1899, i, 620) analyses, indicating the presence in oil of neroli of 10—20 per cent., and in oil of petit grain of 50—70 per cent., of esters calculated as linalyl acetate, are confirmed by the examination of a number of oils distilled in May, 1899. The yield of oil of neroli increased towards the end of the month, the weather being fine, but was diminished in wet weather; this variation is the reverse of that observed with oil of rose, larger yields of which are obtained in wet weather. The proportion of esters appears to be independent of the origin of the flowers. Some experiments are described which show that 5—6 per cent. of the esters contained in oil of neroli are hydrolysed when the oil is prepared by distillation. N. L.

**Preparation of Gentiopicroin, the Glucoside of Fresh Gentian Root.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 131, 113—115).—The fresh gentian root is cut into small pieces and quickly dropped into boiling alcohol in order to destroy the oxidising and hydrolytic ferments which would otherwise lead to loss of the glucoside. The liquid is boiled for 30 mins. in a reflux apparatus, cooled, filtered, the alcohol removed by evaporation, and the residual liquid mixed with chalk, again filtered, evaporated to a syrup, and left to crystallise for a fortnight. The mass of needles thus obtained is recrystallised from a mixture of equal volumes of chloroform and 95 per cent. alcohol. The rotatory power of gentiopicroin in 2 per cent. aqueous solution was found to be  $[\alpha]_D - 196^\circ$ . N. L.

**Glucosides Containing Thiocarbimides.** By H. TER MEULEN (*Rec. Trav. Chim.*, 1900, 19, 37—45).—By distilling large quantities of *Tropaeolum majus* in steam, Hofmann obtained benzyl cyanide (Abstr., 1874, 792). Gadamer (Abstr., 1899, i, 930, and this vol., i, 49), working on a large scale, noticed the production of both benzyl cyanide and benzyl thiocarbimide, whilst smaller quantities of the plant yielded only the latter compound.

The author is of opinion that the cyanide is not present in the glucoside, but that it is produced by the prolonged action of boiling water on the thiocarbimide. The thiocarbimides have a characteristic toxic action on *Saccharomyces mycoderma*, whereas this organism is not affected by benzyl cyanide, cyanates, or organic sulphides. This reaction may be employed in detecting a thiocarbimide, and also in estimating the amount of this substance present in a solution. On adding to a culture of *S. mycoderma* in beer a solution of benzyl-

thiocarbimide which has been previously heated at  $100^{\circ}$  for 4 hours, it is found that the diminution of physiological activity corresponds with the decomposition of 90 per cent. of the thiocarbimide. The glucoside of *T. majus* has no physiological activity, the toxic action being only manifested after its hydrolysis either by the enzyme of the plant or by myrosin. Diastase and emulsin do not decompose this glucoside.

The leaves of *Cochlearia officinalis* and *Cardamine pratensis*, the roots of *Reseda odorata*, *Cochlearia armoracia*, and *Isatis tinctoria*, and the seeds of the black and white radish and several varieties of *Brassica* contain thiocarbimides in the form of glucosides, accompanied by enzymes apparently identical with myrosin. G. T. M.

**Aloins.** By EUGÈNE LÉGER (*Compt. rend.*, 1900, 131, 55—58).—After seven crystallisations from methyl alcohol, barbaloin no longer gives Klunge's reaction with copper sulphate and sodium chloride, although the development of a red coloration was formerly considered to be a distinctive test for this aloin. On the other hand, *isobarbaloin* readily develops a violet-red coloration, and the reaction may be employed in removing the last traces of this substance from barbaloin.

A hot aqueous solution of barbaloin containing a small amount of *isobarbaloin* is treated with excess of copper sulphate and sodium chloride until the crystals which separate on cooling no longer give the colour reaction; the product consisting of pure barbaloin is then recrystallised from methyl alcohol.

The triacetyl derivative of pure trichlorobarbaloin melts at  $164.8^{\circ}$ , whereas specimens contaminated with the corresponding derivative of *isobarbaloin* melt at  $152—153^{\circ}$ .

*Tribromobarbaloin*,  $C_{10}H_{13}Br_3O_7 \cdot 3H_2O$ , formed by the action of bromine water on pure barbaloin, crystallises from dilute alcohol in yellow needles; it differs in appearance, solubility, and water of crystallisation from the ordinary so-called "tribromobarbaloin," which in reality is tribromo*isobarbaloin*.

The least soluble constituent of the aloins from Cape aloes is identical in every respect with pure barbaloin. G. T. M.

**Nature of Klunge's Aloin Reaction and the Oxidising Action of Cupric Salts in Presence of Cyanogen Compounds.** By EDUARD SCHÄER (*Arch. Pharm.*, 1900, 238, 279—298).—The violet-red coloration exhibited by solutions of aloes in presence of copper sulphate and hydrocyanic acid is also developed by other cupric salts, including the oxide, and by the thiocyanates, ferrocyanides, alkyl cyanides, natural and synthetical alkylthiocarbimides, and haloid salts; the colour-tone is purest when a very dilute solution of the copper salt is used. On only one occasion did the 'aloin-red' separate in a solid form as an amorphous, carmine-red precipitate; it is only very slightly soluble in water and in most organic solvents, but dissolves in alcohol, aqueous ammonia, and quite readily in a strong solution of chloral hydrate; in the pure state, it is fairly stable, although the crude solution very rapidly decomposes.

'Aloin-red' appears to be produced as one stage in the spontaneous oxidation of aloin solutions in air at the ordinary temperature or on a water-bath, but the colour is not developed by air that has been

ozonised with moist phosphorus, or in presence of bitter almond oil; metallic and colloidal mercury and colloidal platinum cause a rapid development of the red coloration, and iodine, unlike chlorine and bromine, has a similar action; nitrous acid, permanganate, ferrocyanide, and nitroprusside give 'aloin-red,' but chromic acid and hypochlorites are indifferent; silver nitrate acts gradually, but mercuric nitrate not at all; the higher oxides of manganese, nickel, and cobalt give the red coloration.

'Aloin-red' is reduced by a large number of agents, including some peroxides. When its solutions are kept, a sediment gradually deposits which, when crystallised from toluene, is obtained in minute, orange-yellow needles, and shows the reactions of alochrysine.

T. M. L.

**Colouring Matter of Annatto.** By KARL G. ZWICK (*Arch. Pharm.*, 1900, 238, 58—80. Compare Etti, *Abstr.*, 1878, 739).—No colouring matter ("orellin") is to be found in annatto. The bixin could not be obtained crystalline by Etti's method; a surer means (*Abstr.*, 1897, i, 630) is repeated extraction, alternately with chloroform and light petroleum, in the former of which it is soluble, whilst insoluble in the latter. It melts at  $189^{\circ}$  to a reddish liquid. Its formula,  $C_{23}H_{34}O_5$ , can perhaps be resolved into  $OMe \cdot C_{27}H_{29}(\cdot O)_2(OH)_2$ , for it contains one methoxyl group, and yields a diphenylhydrazone and a dipotassium salt; it could not, however, be made to form an acetate or benzoate. No conclusive result could be obtained by reduction with sodium in moist ether, or by distillation with zinc dust in a current of hydrogen gas, or by zinc and acetic acid; by oxidation with potassium permanganate, or potassium dichromate and acetic acid, or nitric acid (in which case a nitro-compound appears to be formed, and not oxalic acid); by fusion with potassium hydroxide or by distillation with lime. On the other hand, palmitic acid was obtained by distilling either bixin or annatto itself with superheated steam. C. F. B.

**Alkaloids Present in the Seeds of Anagryis Fœtida.** By ERNST SCHMIDT (*Arch. Pharm.*, 1900, 238, 184—191).—An introductory survey of the facts recorded in the two following abstracts. A report by Hans Meyer as to the physiological activity of anagryine hydrobromide is appended showing that the latter is very different in its action from cytisine, for whilst cytisine, like strychnine, produces convulsions, anagryine has little more effect on a dog than to enhance reflex excitability. W. A. D.

**Anagryine.** By F. M. LITTERSCHEID (*Arch. Pharm.*, 1900, 238, 191—227. Compare Klostermann, *Abstr.*, 1899, i, 959, and following abstract).—Anagryine, prepared by Partheil and Spasski's method (*Apoth. Zeit.*, 1895, 10, 903) from the seeds of *Anagryis fœtida*, is always contaminated by more or less cytisine; the pure alkaloid is best obtained by adding an excess of phenylthiocarbamide to an alcoholic solution of the crude substance, and, after three days, collecting the precipitate of the insoluble cytisine phenylthiocarbamide thus formed (this vol., i, 516). The filtrate, on evaporation to a syrupy consistence, yields on extracting with dilute hydrochloric acid

a solution from which pure anagyryne can be obtained by adding alkali and extracting the liberated base with chloroform. A careful examination of the seeds of *Anagyris fetida* shows that they contain no other alkaloid beside cytisine and anagyryne, the ratio in which these substances occurs varying from 3 : 1 to 3 : 2.

The early part of the paper confirms most of the statements made by Klostermann (*loc. cit.*) with regard to anagyryne; the following facts are, however, new. Anagyryne mercurichloride crystallises from water containing hydrochloric acid and mercuric chloride in three forms: (1), with  $\frac{1}{2}\text{H}_2\text{O}$ ; aggregates of large, transparent, colourless prisms, melting at  $225\text{--}226^\circ$ ; (2), sheaves of anhydrous, slender, white needles, melting indefinitely at  $213\text{--}214^\circ$ ; (3), white, nodular crystals melting at  $231^\circ$  (compare Klostermann). *Anagyryne hydriodide*,  $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{HI}\cdot\text{H}_2\text{O}$ , crystallises from alcohol in stellar aggregates of yellow needles, and does not melt at  $250^\circ$ ; of the *periodides*, (1),  $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{HI}\cdot\text{I}$ , forms beautiful, lustrous, brownish-red needles; (2),  $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{HI}\cdot\text{I}_2$ , forms steel-grey, lustrous needles or plates, and is unstable, evolving iodine.

*Anagyryne methochloride aurichloride*,  $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{MeCl}\cdot\text{AuCl}_3$ , prepared by adding auric chloride to the solution obtained on decomposing anagyryne methiodide with silver chloride, melts at  $198\text{--}199^\circ$ ; the *platinichloride*,  $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{MeHPtCl}_3\cdot\text{H}_2\text{O}$ , forms small, yellowish-red needles. *Anagyryne ethiodide*,  $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{EtI}\cdot\text{H}_2\text{O}$ , forms brittle, yellow needles; the salt,  $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{EtCl}\cdot\text{AuCl}_3$ , is amorphous.

Boiling acetic anhydride in presence of anhydrous sodium acetate is without action on either anagyryne or cytisine, showing that in neither alkaloid is a hydroxyl group present.

Anagyryne on treatment with cold 10 per cent. aqueous barium permanganate yields an *oxide*,  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2$ , by loss of 1 mol. of hydrogen and the addition of 1 atom of oxygen; it crystallises from chloroform, on adding light petroleum, in large, silky needles, or stellar aggregates of smaller needles, melts at  $195^\circ$ , and is levorotatory both in aqueous and in hydrochloric acid solution. It reddens blue litmus although, as a base, it yields an *aurichloride*,  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HAuCl}_4$ , which crystallises from alcohol in dark golden-yellow, transparent, rhombic prisms, and melts at  $225^\circ$ ; the *platinichloride*,  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$ , crystallises from water in stellar aggregates of needles and melts and decomposes at  $240^\circ$ ; the *mercurichloride*,  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HCl}\cdot\text{HgCl}_2$ , forms monoclinic (3), lustrous, colourless prisms, and melts at  $226\text{--}227^\circ$ .

Acetic anhydride and benzoic anhydride are without action on anagyryne oxide, and the same is true of hydroxylamine; the oxide thus contains neither hydroxylic nor carbonylic oxygen. Since, also, it fails to interact with zinc and hydrochloric acid, or with sulphurous acid, it does not appear to contain its added oxygen combined with quinquivalent nitrogen as in the oxides of tertiary aromatic bases (Merlin, *Abstr.*, 1893, i, 113; Wernick and Wolfenstein, *Abstr.*, 1898, i, 536).<sup>\*</sup> It is a tertiary base since it is not acted on by nitrous acid, but further research will be necessary to establish its nature.

<sup>\*</sup> Compare also Bamberger and Tschirner, *Abstr.*, 1899, i, 347, 682.—W. A. D.



Since a comparison of anagryne and cytisine appears to indicate that the former is a butyleytisine, the action on cytisine of *n*-, *iso*-, *sec*-, and *tert*-butyl iodides, both alone and in presence of the corresponding alcohol, at temperatures of 100° and 150°, was studied, but in nearly all cases no action occurred; *isobutyl* bromide and *tert*-butyl chloride also gave negative results. On heating *isobutyl* iodide and cytisine, however, with alcoholic potassium hydroxide for 3 hours at 100°, *isobutyleytisine* appears to be formed in small quantity; it was isolated as the *platinichloride*,  $C_4H_9 \cdot C_{11}H_{13}ON_2 \cdot H_2PtCl_6 \cdot 1\frac{1}{2}H_2O$ , in the form of dark red, transparent needles, darkening at 230°, and decomposing at about 250°. A *sec-butyleytisine platinichloride* crystallising with  $3H_2O$  in reddish-yellow crystals, and with  $1\frac{1}{2}H_2O$  in four-sided plates, was also obtained; but in this case, as with the *isobutyl* compound, insufficient salt was isolated to enable a definite comparison with anagryne *platinichloride* to be made.

The action of *sec*-butyl iodide on methyleytisine under different conditions was also studied, but in every case a negative result was obtained.

W. A. D.

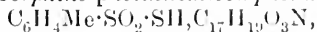
**Anagryne.** By MAX KLOSTERMANN (*Arch. Pharm.*, 1900, 238, 227—230).—The facts dealt with in this paper have already appeared (*Abstr.*, 1899, i, 959).

W. A. D.

**Arginine.** By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1900, 29, 329—333).—Gulewitsch is of opinion that the arginine he has prepared from animal sources is different from 'vegetable arginine.' The present paper shows that this is not the case; the differences noted are all explicable on other grounds.

W. D. H.

**Alkylthiosulphonates of Organic Bases.** By JULIUS TROEGER and OTTO LINDE (*Arch. Pharm.*, 1900, 238, 4—8).—When a potassium alkylthiosulphonate is mixed with the hydrochloride of an alkaloid in aqueous solution, the alkylthiosulphonate of the alkaloid is precipitated; it may be recrystallised from water if necessary. In this way, the following salts were prepared: *Berberine p-toluenethiosulphonate*,  $C_6H_4Me \cdot SO_2 \cdot SH, C_{20}H_{17}O_4N, H_2O$ ;  *$\beta$ -naphthalenethiosulphonate*,  $C_{10}H_7 \cdot SO_2 \cdot SH, C_{20}H_{17}O_4N$ ; the benzene- and  $\alpha$ -naphthalenethiosulphonates were prepared, but not analysed; all these are yellow in colour. *Morphine p-toluenethiosulphonate*,



and the benzene- and  $\beta$ -naphthalene-thiosulphonates were prepared; the two last were not analysed. *Strychnine p-toluenethiosulphonate*,  $C_6H_4Me \cdot SO_2 \cdot SH, C_{21}H_{22}O_2N_2$ .

The precipitation of berberine by potassium  $\beta$ -naphthalenethiosulphonate is complete, and may be utilised for the estimation of the alkaloid. A dilute aqueous solution of the thiosulphonate is prepared and standardised by titration with *N*/100 iodine with starch as indicator; the berberine is precipitated with an excess of this solution, and the excess estimated by titrating the filtered solution with the iodine.  $2I = 2C_{10}H_7 \cdot SO_2 \cdot SK = 2C_{20}H_{17}O_4N$ .

C. F. B.

**Action of Phenylthiocarbimide on Cytisine, Carpaine, and Conhydrine.** By F. M. LITTSCHIED (*Arch. Pharm.*, 1900, 238, 230—240).—Cytisine, as a secondary base, interacts quantitatively with phenylthiocarbimide in alcoholic solution at the ordinary temperature, to yield the *phenylthiocarbamide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{N}\cdot\text{C}_{11}\text{H}_{13}\text{ON}$ , which crystallises from concentrated alcohol in colourless prisms or opaque, white needles, and melts at  $254^\circ$ ; it is basic in character and yields an *aurichloride*, a *platinichloride*, and a *mercurichloride*, but these could not be obtained pure. It is only partially resolved into phenylthiocarbimide and cytisine by hydrochloric acid (either 25 per cent. or fuming, at the ordinary temperature or at  $100^\circ$ ), dilute sulphuric acid, or aniline; in each case, the cytisine isolated was the ordinary *lævo*-variety, no racemisation having occurred. Attempts to convert the phenylthiocarbamide into the corresponding cytisine phenylcarbamide by means of yellow mercuric oxide gave only a trace of a colourless compound, crystallising from ethyl acetate in plates and melting at  $146$ — $147^\circ$ ; not enough was obtained for analysis.

*Carpaine phenylthiocarbamide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{N}\cdot\text{C}_{14}\text{H}_{24}\text{O}_2$ , crystallises from absolute alcohol in sheaves of needles, melts at  $107^\circ$ , and is much more easily decomposed than the analogous cytisine derivative; thus auric chloride in the cold regenerates carpaine.

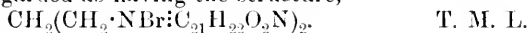
With conhydrine, owing to the small amount of material at the author's disposal, no definite result was obtained. W. A. D.

**Carnosine, a New Base present in Meat Extract.** By WLADIMIR VON GULEWITSCH and S. AMIRADŽIBI (*Ber.*, 1900, 33, 1902—1903).—The isolation of a new base, *carnosine*,  $\text{C}_9\text{H}_{14}\text{O}_3\text{N}_4$ , from Liebig's extract of beef, is described; it is very soluble in water, has a strongly alkaline reaction in solution, forms microscopic needles, and melts and decomposes at  $239^\circ$ . The *nitrate*,  $\text{C}_9\text{H}_{15}\text{O}_6\text{N}_5$ , crystallises from water on adding alcohol in beautiful, stellar aggregates of soft needles, melts and decomposes at  $211^\circ$ , and has  $[\alpha]_D + 22.3^\circ$  at  $20^\circ$ . The *copper* derivative,  $\text{C}_9\text{H}_{14}\text{N}_4\text{O}_4\text{Cu}$ , obtained by boiling the base with copper carbonate, crystallises from water in microscopic, six-sided, hexagonal plates, and decomposes without melting at  $220^\circ$ . The *silver* derivative of carnosine and the acid double salt obtained with silver nitrate closely resemble the corresponding derivatives of arginine. W. A. D.

**Morphine.** By ALFRED PARTHEIL and A. GRONOVER (*Arch. Pharm.*, 1900, 238, 161—163).—The statement of Hesse (*Abstr.*, 1884, 613) and of Knorr (*Abstr.*, 1889, 417), that methylmorphimethine methohydroxide yields trimethylamine on heating at  $170$ — $180^\circ$  is confirmed; the base isolated was characterised by its *platinichloride*, which melts and decomposes somewhat indefinitely at  $220^\circ$  (Knorr, *loc. cit.*, gives  $240$ — $245^\circ$ ), and by its *aurichloride*, which melts at  $231$ — $231.5^\circ$  (Knorr gives  $253^\circ$ ; Zay, *Abstr.*, 1884, 286, gives  $220^\circ$ ). From Vongerichten and Schroetter's results (*Abstr.*, 1882, 1112), it would be expected that dimethylpropylamine would be the decomposition product of methylmorphimethine methohydroxide rather than trimethylamine. W. A. D.

**Derivatives of Strychnine.** By P. J. TROWBRIDGE (*Arch. Pharm.*, 1900, **238**, 241—253).—Strychnine bromoethyl bromide,  $C_{21}H_{22}O_2N \cdot NBr \cdot C_2H_4Br$  (Ménétriers, *J. pr. Chem.*, 1862, **85**, 230), can be readily converted into the chloride by shaking with freshly precipitated silver chloride; the *aurichloride*,  $C_{21}H_{22}O_2N_2(C_2H_4Br)AuCl_4$ , forms a yellow precipitate, the *mercurichloride* a white, crystalline precipitate. Strychnine vinyl hydroxide forms a yellow *aurichloride*,  $C_{21}H_{22}O_2N_2(C_2H_3)AuCl_4$ , and a white, crystalline *mercurichloride*; the *nitrate*,  $C_{21}H_{22}O_2N_2(C_2H_3)NO_3$ , forms yellowish-white, silky needles, dissolves slightly in cold, but readily in hot water, begins to darken at  $250^\circ$ , and blackens without melting at  $280^\circ$ . By the action of chlorine water on strychnine vinyl chloride, the *additive* compound,  $C_{21}H_{22}O_2N_2(C_3H_3Cl_2)Cl$ , is produced, but when chlorine gas is used substitution also takes place. By the action of moist silver oxide on the base a certain amount of strychnine is regenerated, but vinylstrychnine is not produced.

Propylene bromide does not combine with strychnine even at  $150^\circ$ , but merely gives a hydrobromide. Trimethylene bromide, however, reacts at the atmospheric temperature and gives an *additive* compound,  $2C_{21}H_{22}O_2N_2 \cdot C_3H_6Br_2$ , which crystallises from dilute alcohol in white needles containing  $4H_2O$ , and melts at  $297^\circ$ . The *chloride*,  $2C_{21}H_{22}O_2N_2 \cdot C_3H_6Cl_2$ , prepared by the action of silver chloride on the bromide, forms white needles readily soluble in water; the *platinichloride* is reddish-yellow and the *aurichloride* lemon-yellow; the *chromate* is a yellow, crystalline precipitate; the *nitrate*,  $2C_{21}H_{22}O_2N_2 \cdot C_3H_6(NO_3)_2$ , forms colourless, transparent needles, and the *sulphate*,  $2C_{21}H_{22}O_2N_2 \cdot C_3H_6SO_4$ , white flakes. The additive compound of strychnine and trimethylene bromide, unlike that formed from strychnine and ethylene bromide, is thus the dibromide of a diacid base and is regarded as having the structure,



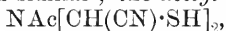
**Action of Sulphur Dioxide and Hydrogen Sulphide on Pyridine.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1900, **130**, 1714—1716. Compare Abstr., 1898, ii, 501).—The *compound*,  $C_5NH_5 \cdot SO_2$ , produced by the direct union of dry sulphur dioxide and pyridine, forms yellow, deliquescent lamellæ which readily undergo decomposition. When zinc is placed in contact with pyridine saturated with sulphur dioxide, the metal becomes gradually covered with a white deposit which dissolves in hydrochloric acid with liberation of sulphur dioxide and sulphur; the filtrate from a suspension of this white substance in a saturated solution of hydrogen sulphide, when evaporated in a vacuum, deposits a crystalline substance having a composition corresponding with that of a pyridine trithionate,  $(C_5NH_5)_2 \cdot H_2S_3O_6$ .

*Pyridine tetrathionate*,  $(C_5NH_5)_2 \cdot H_2S_4O_6$ , prepared by saturating pyridine successively with sulphur dioxide and hydrogen sulphide, treating the product with alcohol, and allowing the filtered extract to crystallise, separates in colourless, deliquescent lamellæ which dissolve in water or alcohol; at  $135^\circ$ , it melts to a clear liquid which rapidly turns yellow and evolves sulphur dioxide. The solution obtained by decomposing the tetrathionate with well cooled dilute potassium

hydroxide solution deposits only potassium trithionate and traces of sulphur.

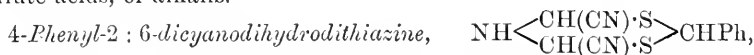
*Pyridine trithionate*,  $(C_5NH_5)_2, H_2S_3O_6$ , obtained in transparent crystals when sulphur dioxide and hydrogen sulphide are passed into a mixture of pyridine with its own weight of water, dissolves in water or alcohol and decomposes at  $105^\circ$ , giving off sulphur dioxide. G. T. M.

**Chrysean.** By GUSTAF HELLSING (*Ber.*, 1900, 33, 1774—1781. Compare Abstr., 1899, i, 563).—When heated, chrysean darkens at  $200^\circ$  and melts and decomposes at  $204^\circ$ ; it is decomposed also when boiled with dilute acids or alkalis, and is oxidised by nitric acid to sulphuric and oxalic acids. With potassium permanganate, oxalic acid and sulphur are obtained, whilst with potassium ferricyanide or ferric chloride amorphous products are formed, and the same holds true with chlorine, bromine, or iodine. The *copper* derivative of chrysean,  $Cu(C_4H_4N_3S_2)_2$ , forms microscopic, olive-brown prisms, and crystallises from water, with  $4H_2O$ , in slender, bright brown needles; the *mercurichloride*,  $C_4H_5N_3S_2, HgCl_2$ , forms lustrous, yellowish-brown needles, and the *picrate* is similar; the *acetyl* derivative,



crystallises from alcohol, in which it is easily soluble, in small, four-sided, lustrous, golden plates, begins to decompose at  $214^\circ$  and melts at  $237^\circ$ .

Chrysean condenses with aldehydes to form substances of the type,  $NH \begin{smallmatrix} \text{CH(CN) \cdot S} \\ \text{CH(CN) \cdot S} \end{smallmatrix} CHR$ , derived from the nucleus,  $NH \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{S} \end{smallmatrix} CH_2$ , to which the name *dihydrodithiazine* is assigned; aromatic ketones, however, are without action on chrysean, although acetone yields a crystalline derivative. The condensation products are relatively unstable, being resolved into their components on boiling with water, dilute acids, or alkalis.



obtained by warming benzaldehyde (1 mol.) with chrysean in alcoholic solution, crystallises from alcohol in golden scales and melts and decomposes at  $183$ — $184^\circ$ .

4-p-isoPropylphenyl-2 : 6-dicyanodihydrodithiazine,  $C_{14}H_{15}N_3S_2$ , obtained similarly by using cumaldehyde, crystallises from alcohol in small, slender, yellow needles and melts and decomposes at  $118^\circ$ . Salicylaldehyde yields 4-o-hydroxyphenyl-2 : 6-dicyanodihydrodithiazine,  $C_{11}H_9ON_3S_2$ , which crystallises in long, lustrous, golden needles and melts and decomposes at  $187^\circ$ ; the analogous *furfuryl* derivative forms small, four-sided, brown scales and melts and decomposes at  $184^\circ$ . Chrysean dissolved in acetic anhydride interacts vigorously with acetone to form 1-acetyl-4 : 4-dimethyl-2 : 6-dicyanodihydrodithiazine, which forms brown scales and melts and decomposes at  $216^\circ$ .

The silver and lead derivatives of chrysean are unstable, readily giving rise to the corresponding metallic sulphide and a derivative of azthiotetride,  $CH_2 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} CH$ .

2:4-Dicyanodihydroazthiotetride,  $\text{NH} \begin{smallmatrix} \text{CH}(\text{CN}) \\ \text{CH}(\text{CN}) \end{smallmatrix} \text{S}$ , obtained by boiling chrysean suspended in water with silver sulphate, separates in slender, felted, yellowish-white needles which melt at  $103^\circ$ , and rapidly become red owing to the action of light; it yields a white, crystalline double salt,  $\text{C}_4\text{H}_3\text{N}_3\text{S}, \text{AgNO}_3$ , with silver nitrate, a bright yellow mercurichloride, and an acetyl derivative,  $\text{NAc}[\text{CH}(\text{CN})]_2\text{S}$ , which crystallises from alcohol in lustrous, white needles. With hydroxylamine, it yields the aminoxime,  $\text{CN} \cdot \text{C}_2\text{H}_3\text{NS} \cdot \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{OH}$ , which crystallises from alcohol in bright yellow needles and explodes at  $166^\circ$ ; the foregoing acetyl derivative similarly yields 2-cyano-1-acetyldihydroazthiotetride-4-aminoxime, which crystallises in short, bright yellow, rhombic prisms, and melts and decomposes at  $218^\circ$ . The diacetyl derivative,  $\text{CH}(\text{CN}) \begin{smallmatrix} \text{NAc} \\ \text{S} \end{smallmatrix} \text{CH} \cdot \text{C}(\text{NHAc}) \cdot \text{N} \cdot \text{OH}$ , prepared from 2-cyanodihydroazthiotetride-4-aminoxime, forms slender, bright yellow needles; it melts at  $94^\circ$  and, after solidification, at  $165^\circ$ , but after again solidifying it melts and decomposes at  $237^\circ$ . The triacetyl derivative,  $\text{CH}(\text{CN}) \begin{smallmatrix} \text{NAc} \\ \text{S} \end{smallmatrix} \text{CH} \cdot \text{C}(\text{NHAc}) \cdot \text{N} \cdot \text{OAc}$ , crystallises in transparent rhombohedra, melts at  $170^\circ$ , and after solidifying melts and decomposes at  $230^\circ$ . W. A. D.

Quinoline Methiodide. By WILHELM MARCKWALD and ERWIN MEYER (*Ber.*, 1900, 33, 1884).—Since great pressure is generated within the sealed vessel used for preparing quinoline methiodide by La Coste's method (*Abstr.*, 1882, 980), and since this is often accompanied by an explosion, the methiodide is more conveniently obtained in quantity by carrying out the reaction in an open vessel fitted with a reflux apparatus. The substance formerly described as quinoline methiodide (m. p.  $72^\circ$ ) is in reality the hydrate,  $\text{C}_{10}\text{H}_9\text{NI}, \text{H}_2\text{O}$ ; the anhydrous substance melts at  $133^\circ$  and crystallises unchanged from absolute alcohol, but from dilute alcohol the foregoing hydrate separates. W. A. D.

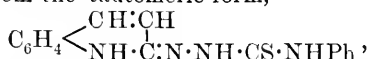
2-Quinolylhydrazine and its Derivatives. By WILHELM MARCKWALD and ERWIN MEYER (*Ber.*, 1900, 33, 1885—1895).—2-Quinolylhydrazine,  $\text{C}_9\text{NH}_6 \cdot \text{NH} \cdot \text{NH}_2$ , prepared by heating 2-chloroquinoline with an excess of hydrazine hydrate for 6 hours at  $140^\circ$ , separates from water or benzene in large crystals and melts at  $134$ — $135^\circ$ ; it is a monacid base, and yields easily soluble salts. The platinichloride,  $(\text{C}_9\text{H}_9\text{N}_3)_2, \text{H}_2\text{PtCl}_6$ , and the picrate,  $\text{C}_{17}\text{H}_{12}\text{N}_6\text{O}_7$ , form sparingly soluble crystals and melt and decompose at  $170^\circ$  and  $187^\circ$  respectively.

Benzylidene-2-quinolylhydrazine,  $\text{C}_9\text{NH}_6 \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$ , forms yellow crystals, melts at  $151^\circ$ , and yields a sparingly soluble platinichloride melting at  $185$ — $186^\circ$ , a dichromate melting and decomposing at  $220^\circ$ , and a picrate melting at  $198^\circ$ . When 2-quinolylhydrazine is left with ethyl oxalate dissolved in alcohol for several hours in the cold, the hydrazide,  $\text{C}_9\text{NH}_6 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , separates in yellow, feathery crystals melting at  $174$ — $175^\circ$ ; at  $150^\circ$ , ocal-di-2-quinolylhydrazide,  $\text{C}_2\text{O}_2(\text{NH} \cdot \text{NH} \cdot \text{C}_9\text{NH}_6)_2$ , is obtained as a white, sparingly soluble, crystalline powder melting at  $251^\circ$ .

2-Quinolylsemicarbazide,  $C_9NH_6 \cdot NH \cdot NH \cdot CO \cdot NH_2$ , obtained by digesting 2-quinolylhydrazine hydrochloride with aqueous potassium cyanate at  $100^\circ$ , forms nodular crystals and melts at  $202^\circ$ ; the *platinichloride* and *picrate* are sparingly soluble, the latter melting at  $189^\circ$ .

The *phenylthiosemicarbazide*,  $C_9NH_6 \cdot NH \cdot NH \cdot CS \cdot NHPh, H_2O$ , obtained by dissolving phenylthiocarbimide and 2-quinolylhydrazine in 95 per cent. alcohol, forms yellowish crystals, melts at  $106^\circ$ , subsequently resolidifies, and finally melts again at  $260^\circ$ ; the anhydrous phenylthiosemicarbazide, prepared by carrying out the same condensation in dry benzene, forms dark yellow crystals which melt initially at  $144^\circ$ , finally at  $260^\circ$ , and absorb moisture from the air to form the foregoing hydrate; the *picrate* melts at  $168$ — $169^\circ$ . The substance melting at  $260^\circ$ , formed on heating either phenylthiosemicarbazide or its hydrate above the melting point, appears to be a

naphtriazolylmercaptan,  $\begin{array}{c} CH:CH:C:N \\ | \quad | \quad | \\ C_6H_4-N-C-SH \end{array}$ , formed by the loss of aniline (1 mol.) from the tautomeric form,



of the parent thiosemicarbazide. When heated with dilute nitric acid, the mercaptan loses its sulphur (compare Wohl and Marekwald, Abstr., 1899, 624, 866), and yields the *nitrate* of naphtriazole,

$\begin{array}{c} CH:CH:C:N \\ | \quad | \quad | \\ C_6H_4-N-CH \end{array}$ , in the form of colourless crystals melting at  $202^\circ$ .

Naphtriazole, obtained by the action of concentrated alkali hydroxides on the nitrate, crystallises from water in long, white needles, and melts at  $175^\circ$ ; it is best prepared by boiling 2-quinolylhydrazine with anhydrous formic acid. The 2-quinolylhydrazine here behaves as its

tautomeride,  $\begin{array}{c} CH:CH:C:N \cdot NH_2 \\ | \quad | \\ C_6H_4-N-NH \end{array}$ ; the alternative configuration,

$C_6H_4 < \begin{array}{c} CH:C:CH:N \\ | \quad | \quad | \\ N-C-NH \end{array}$ , for naphtriazole, derived from the true formula

for 2-quinolylhydrazine, would make it an analogue of indazole, but this view is untenable, since, unlike the latter, it fails to yield a nitroso-derivative with nitrous acid. Naphtriazole is neutral to litmus, and yields salts with an acid reaction in aqueous solution; the *platinichloride*,  $(C_{10}H_7N_3)_2 \cdot H_2PtCl_6$ , forms orange-red crystals and melts at  $323^\circ$ ; the *dichromate* blackens at  $300^\circ$  without melting, whilst the *argentonitrate* forms white crystals, and melts and decomposes at  $239^\circ$ .

Naphtetrazole,  $\begin{array}{c} CH:CH:C:N \\ | \quad | \quad | \\ C_6H_4-N-N \gg N \end{array}$ , is obtained in theoretical amount on adding aqueous sodium nitrite to a cold acetic acid solution of 2-quinolylhydrazine; it forms white crystals, melts at  $157^\circ$ , and is oxidised quantitatively by aqueous potassium permanganate to tetrazole,  $CH_2N_4$ , and carbon dioxide.

2-Hydrazoquinoline,  $N_2H_2(C_9NH_6)_2$ , is always formed in the preparation of 2-quinolylhydrazine, unless a large excess of hydrazine hydrate is present; it differs from the hydrazine in being insoluble in

boiling water, and separates from dilute acetic acid in yellow crystals melting at  $229^{\circ}$ . It is a diacid base; the *dihydrochloride* forms sparingly soluble needles melting at  $263^{\circ}$ , and the *dipicrate* yellow crystals melting and decomposing at  $244^{\circ}$ . The hydrazo-compound is not acted on by stannous chloride or by zinc dust and acetic acid, but is reduced by boiling with zinc dust and hydrochloric acid to 2-aminoquinoline, the *aurichloride* of which melts at  $263^{\circ}$ . 2-Azoquinoline,  $N_2(C_9NH_6)_2$ , obtained by passing nitrogen trioxide into 2-hydrazoquinoline dissolved in 50 per cent. acetic acid, melts at  $230-231^{\circ}$ , sublimes without decomposition, and is a weak base, its salts being decomposed by water; the *dichromate*,  $(C_{15}H_{12}N_4)_2 \cdot H_2Cr_2O_7$ , decomposes at  $300^{\circ}$ , and the *platinichloride*,  $C_{15}H_{12}N_4 \cdot H_2PtCl_6$ , behaves similarly. W. A. D.

**2-Lepidylhydrazine and 4-Quinaldylhydrazine.** By WILHELM MARCKWALD and M. CHAIN (*Ber.*, 1900, 33, 1895—1899. Compare preceding abstract).—2-Lepidylhydrazine,  $C_9NH_5Me \cdot NH \cdot NH_2$ , prepared by heating 2-chlorolepidine with an excess of hydrazine hydrate for 5 hours at  $150^{\circ}$ , crystallises from boiling water, melts at  $145-147^{\circ}$ , and is a monacid base; the *hydrochloride* and *platinichloride* are sparingly soluble in water. The *benzylidene* derivative,  $C_{10}NH_5 \cdot NH \cdot N : CHPh$ , obtained by means of benzaldehyde, forms slender, lustrous crystals, melts at  $150^{\circ}$ , and yields a crystalline *dichromate*,  $(C_{17}H_{15}N_3)_2 \cdot H_2Cr_2O_7$ . With pyruvic acid, 2-lepidylhydrazine yields the *hydrazone*,  

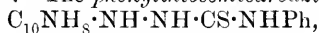
$$C_{10}NH_5 \cdot NH \cdot N : CMe \cdot CO_2H,$$

which melts at  $215^{\circ}$  and crystallises from dilute acid with  $3H_2O$ , the crystals softening completely at  $105^{\circ}$ . 2-Lepidylsemicarbazide, obtained by the interaction of potassium cyanate and 2-lepidylhydrazine hydrochloride, separates from alcohol, in which it is sparingly soluble, in yellow crystals, and melts at  $215^{\circ}$  when rapidly heated. The *phenylthiosemicarbazide*,  $C_{10}NH_5 \cdot NH \cdot NH \cdot CS \cdot NHPh$ , forms yellow crystals, and, when heated at  $180^{\circ}$  (compare *loc. cit.*), loses aniline and yields *methylnaphtriazolylmercaptan*,  $CMe \begin{smallmatrix} \text{CH} - \text{C} : \text{N} : \text{N} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{N} - \text{C} : \text{SH} \end{smallmatrix}$  which is sparingly soluble in all solvents, but separates from alcohol in white crystals melting at  $280^{\circ}$ . *Methylnaphtetrazole*,  $CMe \begin{smallmatrix} \text{CH} - \text{C} : \text{N} : \text{N} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \end{smallmatrix} \text{N}$ ,

forms white crystals and melts at  $207^{\circ}$ . 2-Hydrazolepidine,  $N_2H_2(C_{10}NH_5)_2$ , formed during the interaction of 2-chlorolepidine and hydrazine hydrate, when the latter is not present in excess, is sparingly soluble in all solvents, but separates from very dilute acetic acid in yellow crystals, melts at  $265-270^{\circ}$ , and yields a *dihydrochloride*,  $C_{20}H_{18}N_4 \cdot 2HCl$ , which forms white needles, and is partially dissociated on washing with water; on reduction with zinc dust and hydrochloric acid, the hydrazo-compound yields 2-aminolepidine, and, on oxidation with nitrogen trioxide, 2-azolepidine,  $N_2(C_{10}HN_5)_2$ , which separates from alcohol in vermilion crystals, melts at  $235^{\circ}$ , and yields a crystalline *picrate*. 2-Azolepidine, when heated with hydrochloric acid, is reduced to 2-hydrazolepidine with evolution of chlorine; in this respect it differs from 2-azoquinoline, which is not acted on under the same conditions.

4-Quinaldylhydrazine,  $C_{10}H_{11}N_3$ , is the sole product of the interaction

of 4-chloroquinaldine and hydrazine hydrate at  $150^{\circ}$ , no hydrazo-compound being formed; it crystallises from water in stellar aggregates, melts at  $117-118^{\circ}$ , and yields two crystalline *hydrochlorides*,  $C_{10}H_{11}N_3 \cdot HCl$  and  $C_{10}H_{11}N_3 \cdot 2HCl$ , the latter being converted into the former on heating at  $100^{\circ}$ , or on being kept in a desiccator over potassium hydroxide. *Benzylidene-4-quinaldylhydrazine*,  $C_{17}H_{15}N_3$ , separates from alcohol in yellowish crystals, and melts at  $161-162^{\circ}$ ; its *picrate* melts at  $130^{\circ}$ . *Pyruvic acid 4-quinaldylhydrazone* forms yellow crystals and melts at  $197^{\circ}$ . The *phenylthiosemicarbazide*,



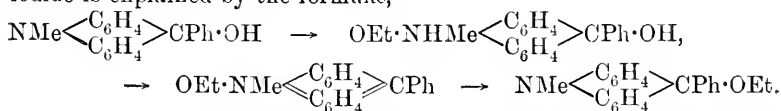
prepared from 4-quinaldylhydrazine, melts at  $139^{\circ}$ .

W. A. D.

**Py-Benzylisoquinolines.** By LEOPOLD RÜGHEIMER (*Ber.*, 1900, **33**, 1719—1720).—By the action of benzaldehyde on benzoyltetrahydroisoquinoline, two compounds are produced, 4-benzylisoquinoline melting at  $117.5-118^{\circ}$ , and 3-benzylisoquinoline melting at  $103.5^{\circ}$ . 1-Benzylisoquinoline is produced by heating isoquinoline with benzyl alcohol at  $300^{\circ}$ , and melts at  $50-52^{\circ}$ .

T. M. L.

**Ammonium Compounds. V. Ammonium Alcoholates.** By HERMANN DECKER (*Ber.*, 1900, **33**, 1715—1718).—The formation of an alcoholate from the pseudo-base obtained from phenylacridine methiodide is explained by the formulæ,



These changes are analogous to those involved in the conversion of the carbinol into salts of the ammonium base, except that the isomeric change of the last stage of the reaction does not take place in the latter case. A similar explanation is given of other analogous cases.

T. M. L.

**Phenyldiimine.** By WILHELM VAUBEL (*Ber.*, 1900, **33**, 1711—1713).—When diazoaminobenzene is reduced with zinc dust in alkaline alcoholic solution, the colouring matter which accompanies it is first destroyed, leaving a pure diazoaminobenzene, which is reduced by further boiling; on acidifying the solution and distilling in a current of steam, *phenyldiimine*,  $NPh \cdot NH$ , is obtained as a yellow oil with a strong odour of bitter almond oil. It has about the same sp. gr. as aniline, boils at  $162-164^{\circ}$  with partial conversion into a solid substance, is only slightly soluble in water, but readily soluble in alcohol, ether, or benzene, is acid rather than basic in its properties, is stable in the air, does not explode on heating or by percussion, does not reduce Fehling's solution, and is highly poisonous, producing cramp. Its mol. wt. is 123 (calc. 106) as determined by Victor Meyer's method at the temperature of boiling aniline.

T. M. L.

**Composition of Compounds of Magenta with Acidic Colouring Matters.** By ALPHONSE SEYEWETZ (*Compt. rend.*, 1900, **130**, 1770—1773. Compare this vol., i, 356).—The following nitro-colouring acids, *o*-nitrophenol, 2:4-dinitrophenol, picric acid, nitrosoresorcinol, and Martius' yellow which contain only nitroxyl and hydroxyl groups



interact with magenta in molecular proportions, whereas naphthol-yellow S, which also contains a sulphonic group, unites with 2 mols. of the colour base.

Diquinonedioxime,  $C_6H_3O_2(N\cdot OH)_2$ , and alizarin-yellow A each combine with 1 mol. of rosaniline, although they contain 2 and 3 hydroxyl groups respectively.

In the phthalein series, both hydroxyl and carboxyl groups take part in the formation of the lake, 1 mol. of uranin, eosin, or erythrosin combining with 2 mols. of the colour base.

Pararosaniline and chrome-blue unite with rosaniline in molecular proportions, whereas 3 mols. of the base are required to saturate 1 mol. of chrome-violet.

The alizarin colouring matters all form salts containing 1 mol. of rosaniline, lakes of this type having been obtained from alizarin, alizarin-red S, alizarin-orange, aminoalizarin, and alizarin-blue.

G. T. M.

**New Blue Dyes of the Thiazine Series.** By W. G. SCHAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 230—248).—When thiodiphenylamine is nitrated, a mixture of mono- and dinitro-derivatives is obtained, which Bernthsen (*Abstr.*, 1886, 53) was unable to separate. The author finds that the mononitro-compound is only slightly soluble in glacial acetic acid, whilst the dinitro-derivative and any unchanged thiodiphenylamine are readily dissolved. By this means the pure *p*-nitrodiphenylamine sulphoxide,  $NO_2\cdot C_6H_3\langle\begin{smallmatrix} NH \\ SO \end{smallmatrix}\rangle C_6H_4$ , is obtained; it separates from acetic acid in thin, sulphur-yellow scales melting and decomposing at  $259^\circ$ . On reduction in hydrochloric acid solution with stannous chloride and tin, this compound yields aminothiodiphenylamine; the double salt of the latter with zinc chloride forms well-developed, lustrous, white needles or plates, which, when dry, are fairly stable, the rapid oxidation of Bernthsen's preparation being probably due to the presence of a diamino-derivative. When the zinc chloride compound of this pure aminothiodiphenylamine is oxidised by means of ferric chloride, iminothiodiphenylimine is obtained, the corresponding double salt of which dissolves in water, giving a pure blue colour; if any diamino-compound were present, a violet coloration would be obtained, due to the formation of thionine (Lauth's violet) in the reduction product. Iminothiodiphenylimine gives a *dichromate*,  $(C_{12}H_8N_2S)_2Cr_2O_7$ , and a *platinichloride*,  $(C_{12}H_8N_2S)_2H_2PtCl_6$ . Koch and Bernthsen's acetyl derivative of thionine (*loc. cit.*) could not be obtained. Iminothiodiphenylimine reacts readily with primary and secondary amines, and less easily with tertiary amines, with the formation of blue dyes. Compounds were obtained with the following amino compounds: Methyl-, ethyl-, and benzyl-amines, aniline, *o*- and *p*-toluidines, *m*-xylidine, *o*-anisidine, *p*-phenetidine, *o*-, *m*-, and *p*-chloroanilines,  $\alpha$ - and  $\beta$ -naphthylamines, diaminoazobenzene, benzidine, dianisidine, tolidine, *m*- and *p*-aminoacetylanilides, *m*-tolylenediamine, methyl-, ethyl-, and benzyl-*m*-tolylenediamines; dimethyl- and diethyl-amines, piperidine, methylaniline, ethylaniline, ethyl-*o*-toluidine, ethyl- and benzyl- $\alpha$ -naphthylamines; trimethylamine, dimethylaniline, diethylaniline, dimethyl-*o*-toluidine, dimethyl-*p*-toluidine. All the bases obtained are blue, the

tints varying from violet to greenish; they dye silk, wool, and cotton, the colours obtained being stable to light, acids, and soap.

*Phenylthionine*,  $N \begin{smallmatrix} \text{C}_6\text{H}_3(\text{NH}) \\ \text{C}_6\text{H}_3(\text{NHPh}) \end{smallmatrix} \text{S}$ , gives, with sodium chloride, potassium nitrate, bromide or iodide, or zinc chloride, crystalline dye-stuffs having metallic lustre; all these salts are readily soluble in hot water, and still more so in alcohol or acetic acid, and the alcoholic solutions do not exhibit fluorescence; they all melt with decomposition, and for the most part contain water of crystallisation. By the action of alkali hydroxide, the salts yield the base, which, with ether or benzene, gives non-fluorescent, carmine-red solutions, whilst it is slightly soluble in water with the formation of a violet colour. The following salts were analysed: the monohydrated *hydrochloride*; the *platinichloride*, which, like the aurichloride, is insoluble in water; and the monohydrated *hydrobromide*, *nitrate*, and *dichromate*.

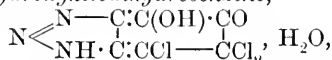
*o-Tolylthionine*,  $\text{C}_{19}\text{H}_{16}\text{N}_3\text{S}$ , combines with salts, forming double compounds which, in aqueous solutions, have a greener tint than the corresponding phenyl derivatives; the *nitrate* crystallises with 1 mol. of water.

*as*-Dimethylthionine, already prepared by Bernthsen (Abstr., 1889, 775) by oxidising dimethylindaminethiosulphonic acid, forms a *platinichloride* and *dichromate*, both readily soluble in hot water. On heating, the dichromate decomposes with the formation of aminothiodiphenylimine dichromate and a compound of the structure  $N \begin{smallmatrix} \text{C}_6\text{H}_3(\text{NH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix} \text{S}$ . From solutions of its salts, cold sodium hydroxide solution precipitates the base, the aqueous solution of which dyes to a violet colour; ethereal solutions of the base have an orange-red colour, with a faint greenish fluorescence. On boiling with sodium hydroxide solution, the base is converted into dimethylthionoline and thionol. T. H. P.

**Ketochlorides and Quinones of Heterocyclic Compounds, and their Products of Change.** Ketochlorides and Quinones of Aziminobenzene. By THEODOR ZINCKE, F. STOFFEL, and E. PETERMANN (*Annalen*, 1900, 311, 276—329. Compare Abstr., 1898, i, 537).—

*Aziminotetrachloroketodihydrobenzene*,  $N \begin{smallmatrix} \text{N} - \text{C} : \text{CCl} \cdot \text{CO} \\ \text{NH} \cdot \text{C} : \text{CCl} \cdot \text{CCl}_2 \end{smallmatrix}$ , prepared from aziminoaminobenzene by the action of chlorine, forms a yellow, viscous oil, but may be obtained in crystals by reduction to aziminotrichlorophenol, followed by chlorination of this compound; it crystallises from benzene in yellowish plates, which become opaque in a vacuum, and melts at  $171^\circ$ , beginning to blacken at  $140^\circ$ .

*Aziminotrichlorohydroxyketodihydrobenzene*,



produced by the action of boiling water on the foregoing substance, forms small, colourless plates, which shrink at  $100^\circ$ , afterwards becoming red, and finally decompose at  $260^\circ$  with detonation; the development of a red colour on heating is due to conversion into aziminodichloro-*o*-quinone, which arises from elimination of water and hydrogen chloride.

*Aziminotrichlorophenol*,  $N \leq \begin{array}{c} \text{N} - \text{C} \cdot \text{CCl} \cdot \text{C} \cdot \text{OH} \\ \text{NH} \cdot \text{C} \cdot \text{CCl} \cdot \text{CCl} \end{array}$ , obtained by reducing aziminotetrachloroketodihydrobenzene with stannous chloride and concentrated hydrochloric acid, crystallises in small, colourless, prismatic needles containing  $1\text{H}_2\text{O}$ , and melts at  $260^\circ$ , becoming anhydrous at  $135^\circ$ ; the *diacetyl* derivative melts above  $300^\circ$ .

*Aziminodichlorophenol*,  $N \leq \begin{array}{c} \text{N} - \text{C} \cdot \text{CCl} \cdot \text{C} \cdot \text{OH} \\ \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CCl} \end{array}$ , is associated with the foregoing substance in the reduction of the tetrachloroketone, and may be obtained by evaporating the mother liquor and precipitating it with water; the compound forms small, colourless needles, which melt and decompose at  $212^\circ$ .

*Aziminodichloro-o-quinone*,  $N \leq \begin{array}{c} \text{N} - \text{C} \cdot \text{CO} \cdot \text{CO} \\ \text{NH} \cdot \text{C} \cdot \text{CCl} \cdot \text{CCl} \end{array}$ , prepared by heating a solution of aziminotrichlorophenol in glacial acetic acid with a small proportion of concentrated nitric acid, is also formed when the tetrachloroketone is heated with water or nitric acid; it crystallises from glacial acetic acid in red needles belonging to the hexagonal system, and gradually blackens when heated, detonating above  $260^\circ$ . As already stated, the quinone is produced when aziminotrichlorohydroxyketodihydrobenzene is heated alone, or with nitric or sulphuric acid. The *azine*,  $\text{C}_{12}\text{H}_5\text{N}_5\text{Cl}_2$ , produced by the action of *o*-phenylenediamine, crystallises from glacial acetic acid in small, yellow needles, and decomposes gradually above  $260^\circ$ .

*Aziminooanilinochlorohydroxy-p-quinone*,  $N \leq \begin{array}{c} \text{N} - \text{C} \cdot \text{CO} - \text{C} \cdot \text{OH} \\ \text{NH} \cdot \text{C} \cdot \text{C}(\text{NPh}) \cdot \text{CCl} \end{array}$ , obtained by heating an alcoholic solution of aziminodichloro-*o*-quinone with aniline, dissolves very sparingly in ordinary solvents, and does not melt below  $300^\circ$ ; hot hydrochloric acid resolves it into the hydrochloride of the aniline derivative of aziminochlorohydroxy-*p*-quinone, which is described below.

*Aziminodichlorocatechol*,  $N \leq \begin{array}{c} \text{N} - \text{C} \cdot \text{C}(\text{OH}) \cdot \text{C} \cdot \text{OH} \\ \text{NH} \cdot \text{C} \cdot \text{CCl} - \text{CCl} \end{array}$ , formed by reducing aziminodichloro-*o*-quinone and aziminotrichlorohydroxyketodihydrobenzene, crystallises from glacial acetic acid in lustrous, white prisms containing 2 mols. of the solvent; it decomposes gradually above  $260^\circ$ . The *acetyl* derivative melts at  $203^\circ$ .

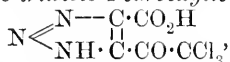
*Aziminochlorohydroxy-p-quinone*,  $N \leq \begin{array}{c} \text{N} - \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{OH} \\ \text{NH} \cdot \text{C} \cdot \text{CO} \cdot \text{CCl} \end{array}$ , prepared by heating aziminooanilinochlorohydroxy-*p*-quinone with alcoholic hydrochloric acid, and treating the resulting aniline compound with boiling water, crystallises from glacial acetic acid in deep yellow, lustrous rhombohedra, which contain acetic acid, and detonates at  $230-231^\circ$ ; the *sodium* salt crystallises in deep violet to reddish-brown needles containing  $2\text{H}_2\text{O}$ , and the *silver*, *copper*, *lead*, *barium*, and *calcium* salts are of the same colour, but insoluble in water. The *anilino*-compound,  $\text{C}_{15}\text{H}_{16}\text{O}_3\text{N}_5\text{Cl}$ , obtained by heating aziminochlorohydroxy-*p*-quinone in alcohol with excess of aniline, crystallises in small, reddish-brown needles, and gives up all its aniline when heated.

Hydrochloric acid converts it into the *hydrochloride* of the anilino-compound,  $C_{12}H_9O_3N_4Cl$ ; this crystallises from glacial acetic acid in groups of golden yellow prisms, which blacken and decompose at  $179^\circ$ . This substance is produced by the action of hydrochloric acid on aziminoanilinochlorohydroxy-*p*-quinone, and, on treatment with boiling water, yields aziminochlorohydroxy-*p*-quinone. *o*-Phenylenediamine does not give rise to the expected eurhodol, but yields two compounds having the composition  $C_{12}H_6ON_5Cl$  and  $C_{18}H_9N_7$  respectively.

*Aziminotetraketotetrahydrobenzene*,  $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO \cdot CO \\ NH \cdot C \cdot CO \cdot CO \end{smallmatrix}$ , produced by the action of concentrated nitric acid on aziminochlorohydroxy-*p*-quinone dissolved in glacial acetic acid, crystallises from glacial acetic acid containing nitric acid in small, transparent, lustrous needles containing  $2H_2O$ , which gradually darken above  $130^\circ$ , and finally detonate at about  $190^\circ$ . The *diazine*,  $C_{18}H_9N_7$ , formed by the action of *o*-phenylenediamine, dissolves very sparingly in ordinary solvents, and does not change below  $260^\circ$ .

*Aziminodihydroxy-p-quinone*,  $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO \cdot C \cdot OH \\ NH \cdot C \cdot CO \cdot C \cdot OH \end{smallmatrix}$ , is prepared by dissolving the tetraketone in a solution of sodium carbonate and passing carbon dioxide through the liquid while heated on the water-bath during a short period, the deep blue solution being then acidified carefully with hydrochloric acid. It crystallises from glacial acetic acid or methyl alcohol as a brick-red powder containing  $1H_2O$ , and does not melt at  $260^\circ$ , although it darkens below this temperature.

*5-Trichloroacetyl-1:2:3-triazole-4-carboxylic acid*,



resulting from the action of bleaching powder on aziminotrichlorophenol, aziminodichloro-*o*-quinone, and aziminochlorohydroxy-*p*-quinone, is best prepared from the dichloroquinone; it separates from wet ether in yellow crystals containing  $3H_2O$ , which become anhydrous at  $100^\circ$ . The *phenylhydrazone* is orange-red, and melts at  $247^\circ$ , when it decomposes.

*5-Trichloroacetyl-1:2:3-triazole*,  $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-CH \\ NH \cdot C \cdot CO \cdot CCl_3 \end{smallmatrix}$ , obtained by heating the carboxylic acid, crystallises from water in slender, colourless needles and melts at  $129^\circ$ . Sodium hydroxide eliminates chloroform, and produces *1:2:3-triazole-4-carboxylic acid*,  $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-CH \\ NH \cdot C \cdot CO_2H \end{smallmatrix}$ , which crystallises from hydrochloric acid in transparent rhombohedra and melts at  $220^\circ$ , when carbon dioxide is eliminated, and *1:2:3-triazole* (*pyrro-a:b-diazole*),  $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-CH \\ NH \cdot CH \end{smallmatrix}$ , produced.

*1:2:3-Triazole-4:5-dicarboxylic* (aziminoethylenedicarboxylic) acid,  $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO_2H \\ NH \cdot C \cdot CO_2H \end{smallmatrix}$ , prepared by the action of a 10 per cent. solution of sodium hydroxide on trichloroacetyl-1:2:3-triazolecarboxylic acid,

has been already obtained by Bladin (Abstr., 1894, i, 76), and by Zincke and Helmert (Abstr., 1896, i, 550); it is also produced during the oxidation of aziminodichloro-*o*-quinone to the tetraketone.

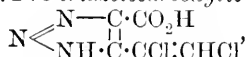
When a 10 per cent. solution of sodium hydroxide acts on aziminodichloro-*o*-quinone, the dichloroketocarboxylic acid, 
$$\text{N} \begin{array}{c} \diagup \text{N} - \text{C} \cdot \text{CO} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{C} \cdot \text{CCl} \cdot \text{CHCl} \end{array}$$
 is produced, crystallising from dilute hydro-

chloric acid in lustrous, colourless needles or stout prisms, which contain  $1\text{H}_2\text{O}$ , and melt, decomposing, at  $165^\circ$ ; the *phenylhydrazone* crystallises from dilute acetic acid in small, yellow needles, which melt and decompose at  $182^\circ$ . The tetrachloroketocarboxylic acid,

$$\text{N} \begin{array}{c} \diagup \text{N} - \text{C} \cdot \text{CO} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{C} \cdot \text{CCl}_2 \cdot \text{CHCl}_2 \end{array}$$
, obtained by the action of chlorine, forms colourless, transparent needles containing  $1\text{H}_2\text{O}$ , and melts at  $167^\circ$ , evolving gas.

The acid,  $\text{C}_6\text{H}_3\text{O}_3\text{N}_3\text{Cl}_2$ , prepared by the action of sodium hydroxide on aziminotetrachloroketodihydrobenzene, crystallises from dilute nitric or glacial acetic acid in lustrous, colourless leaflets which melt and decompose at  $184^\circ$ ; the *phenylhydrazone* crystallises in small, yellow needles, which sinter at  $182^\circ$ , and melt, decomposing, at  $201-203^\circ$ .

*αβ-Dichloroethylene-1:2:3-triazolecarboxylic acid*,



produced on oxidising the foregoing acid with chromic acid or with an alkaline solution of bleaching powder, is also formed when the dichloroketocarboxylic acid from the dichloro-*o*-quinone is oxidised with chromic acid; it forms small, white, lustrous needles, which melt and decompose at  $204-205^\circ$ ; the *silver* salt is white and crystalline.

Chlorine converts the substance into the acid, 
$$\text{N} \begin{array}{c} \diagup \text{N} - \text{C} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{C} \cdot \text{CCl}_2 \cdot \text{CHCl}_2 \end{array}$$
 which crystallises from a mixture of ether and benzene in small, colourless needles and melts and decomposes at  $182^\circ$ ; it also crystallises from dilute nitric acid in leaflets containing  $2\text{H}_2\text{O}$ . M. O. F.

**Aziminole.** By THEODOR ZINCKE and PH. SCHWARZ (*Annalen*, 1900, 311, 329—340. Compare Nietzki and Braunschweig, Abstr., 1895, i, 135).—Benzeneaziminole,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N}(\text{OH}) \end{array} \text{N}$ , obtained by Nietzki and Braunschweig on treating *o*-nitrophenylhydrazine with alkali, melts at  $157^\circ$ ; reduction with hydriodic acid at  $140-150^\circ$  converts it into the *periodide* of aziminobenzene,  $\text{C}_6\text{H}_5\text{N}_3\text{I}_2 \cdot \text{HI}$ . When benzeneaziminole is warmed with acetyl chloride, a *compound* is obtained which is identical with the substance produced by the action of phosphorus trichloride; it melts at about  $110^\circ$ , and probably has the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \\ \diagdown \text{NCl} \end{array} \text{N}$ . The result of treating benzeneaziminole with chlorine is somewhat uncertain, and the composition of the product depends largely on the conditions of the experiment.

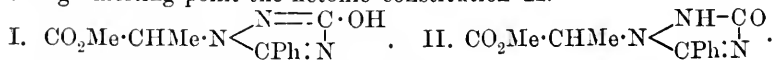
*Aziminolethylenedicarboxylic* [1-hydroxy-1 : 2 : 3-triazole-4 : 5-dicarboxylic] acid,  $\text{N} \begin{smallmatrix} \text{N} \text{---} \text{C} \cdot \text{CO}_2\text{H} \\ \text{N}(\text{OH}) \cdot \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , prepared by oxidising benzene-aziminole with potassium permanganate, separates from water in large, white crystals containing  $2\text{H}_2\text{O}$ ; it melts at  $92^\circ$ , but if previously dried in the desiccator melts and decomposes at  $150^\circ$ . The *monopotassium* salt and the *disilver* salt contain  $1\text{H}_2\text{O}$ , and the *diammonium* salt is anhydrous.

*Tolueneaziminole*,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{N} \text{---} \\ \text{N}(\text{OH}) \end{smallmatrix} \text{N}$ , prepared by the action of alkali on 1 : 3 : 4-nitrotolylhydrazine, crystallises from hot water in long, white needles, and melts at  $176^\circ$ , when it decomposes; the *lead* salt is crystalline, and the *silver* salt amorphous. M. O. F.

**3-Hydroxy-5-alkyl-1 : 2 : 4-triazole-1-propionic Acids.** By JAMES R. BAILEY and S. F. ACREE (*Ber.*, 1900, 33, 1520—1537).—A number of acyl derivatives of ethyl semicarbazinopropionate have been prepared by Widman's method (*Abstr.*, 1898, i, 335). As the other derivatives of semicarbazinopropionic acid are insoluble, or sparingly soluble, in the ordinary organic solvents, they do not lend themselves so readily to the preparation of acyl derivatives, and the yields are mostly poor. The acyl derivatives of the ethyl ester are obtained in almost quantitative yield when the ester is treated with an equivalent quantity of an acid chloride dissolved in benzene, chloroform, or ethyl acetate, generally with the addition of potassium or sodium hydrogen carbonate. Hot concentrated acids remove the acyl groups from these compounds, and dilute alkalis, especially when warm, convert them into the corresponding triazoles.

The 3-hydroxy-5-alkyltriazole-1-propionic acids are dibasic, yielding normal and acid salts, and also monoacetyl derivatives. With diazomethane, they yield methyl methoxytriazolecarboxylates, and when esterified by Fischer's method, give esters which are monobasic acids (phenols), and therefore yield salts and acetyl derivatives.

The colour which the triazole compounds give with ferric chloride varies in different circumstances, a difference which is most readily accounted for by a keto-enolic isomerism. Methyl 3-hydroxy-5-phenyltriazole-1-propionate gives a deep colour with ferric chloride, and when placed in a bath heated at  $157^\circ$ , melts, but then solidifies, to again melt at  $171^\circ$ ; if this variety of high melting point is crystallised from alcohol several times, it melts at  $173\text{--}174^\circ$ , and then gives only the faintest coloration with ferric chloride. It is thought probable that the compound of low melting point has the constitution I, and that of high melting point the ketonic constitution II.



*Ethyl benzoylsemicarbazinopropionate*,

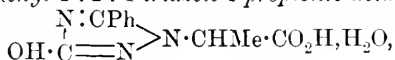


crystallises in hair-like needles, melts at  $177^\circ$ , and is insoluble in ether, benzene, or light petroleum; the *silver* salt,  $\text{C}_{13}\text{H}_{15}\text{O}_4\text{N}_3\text{Ag}_2$ , has been prepared and analysed.

*Benzoylsemicarbazinopropionic acid*, obtained by hydrolysing the

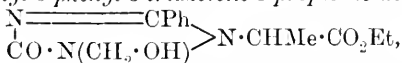
ester with aqueous sodium hydrogen carbonate, crystallises from water in microscopic needles melting and decomposing at  $186^{\circ}$ ; the *sodium* salt,  $C_{11}H_{12}O_4N_3Na$ , is extremely hygroscopic, and decomposes above  $200^{\circ}$ . *Benzoylsemicarbazinopropionitrile* melts and decomposes at about  $185^{\circ}$ .

*3-Hydroxy-5-phenyl-1:2:4-triazole-1-propionic acid*,



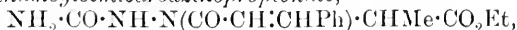
is obtained when any one of the above-mentioned compounds is warmed for some 30 minutes at  $50^{\circ}$  with 10 per cent. potassium hydroxide; it loses its water of crystallisation at  $105-110^{\circ}$ , begins to turn red at  $225^{\circ}$ , melts and decomposes at  $239-240^{\circ}$ , and is insoluble in all the ordinary solvents, with the exception of alcohol. The *barium* (with  $3\text{H}_2\text{O}$ ), *lead*, *ammonium* (with  $\text{H}_2\text{O}$ ), and *calcium* salts have been prepared, also the *hydrochloride*,  $C_{11}H_{11}O_3N_3\cdot\text{HCl}$ , which crystallises in colourless needles melting at  $102^{\circ}$ , and is immediately decomposed by water. The *ethyl* ester,  $\text{OH}\cdot\text{C}_2\text{N}_3\text{Ph}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , melts at  $171-173^{\circ}$ , and is readily hydrolysed by alkalis or by barium carbonate. The *sodium*,  $C_{13}H_{14}O_3N_3Na$ , and *silver* salts have been prepared, as also the *acetyl* derivative melting at  $79^{\circ}$ , the *benzoyl* derivative melting at  $78-79^{\circ}$ , and the *methyl ether*,  $\text{OMe}\cdot\text{C}_2\text{N}_3\text{Ph}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , which is an oil. When treated with alcoholic ammonia, the ethyl ester is converted into *3-hydroxy-5-phenyltriazole-1-propionamide*, crystallising in long, thin needles which turn red at  $240^{\circ}$ , and decompose, with rapid evolution of gas, at  $274^{\circ}$ .

*2-Hydroxymethyl-5-phenyl-3-triazolone-1-propionic acid*,



obtained by the action of formaldehyde on the triazolepropionic acid, crystallises in thin, prismatic plates melting at  $242^{\circ}$  and evolving formaldehyde.

*Ethyl cinnamoylsemicarbazinopropionate*,



is readily soluble in chloroform, alcohol, or ethyl acetate; it softens at  $170^{\circ}$  and melts at  $178-179^{\circ}$ . The corresponding *nitrile* melts and decomposes at  $233^{\circ}$ . *3-Hydroxy-5-styryltriazole-1-propionate* crystallises from alcohol in aggregates of small, glistening needles; it melts and decomposes at  $242-243^{\circ}$ , and, on oxidation with alkaline permanganate, yields benzoic acid. The *acetyl* derivative, melting and decomposing at  $168^{\circ}$ , the *hydrochloride*, and the *ammonium* salt,  $C_{13}H_{12}O_3N_3\cdot\text{NH}_4$ , have been prepared. *Methyl 3-methoxy-5-styryltriazolepropionate*, obtained by the action of an ethereal solution of diazomethane on the acid, is an oil.

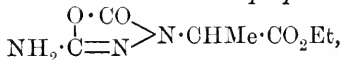
*Ethyl acetylsemicarbazinopropionate* melts at  $141^{\circ}$ , and is soluble in water and the ordinary organic solvents with the exception of ether and light petroleum. The corresponding *nitrile* begins to soften below  $160^{\circ}$ , and melts and decomposes at  $164^{\circ}$ . *3-Hydroxy-5-methyltriazolepropionic acid* turns brown at  $260^{\circ}$ , and is completely decomposed at  $292^{\circ}$ ; it is only very sparingly soluble in water; its *ethyl* ester crystallises in small, flat prisms and melts at  $132^{\circ}$ . The *methyl*

ester, when crystallised from ethyl acetate, melts at 150—151°, and gives a deep colour with ferric chloride; when precipitated by the addition of light petroleum to its ethyl acetate solution, it melts at 154—155°, and does not give so deep a colour with ferric chloride. The *amide* crystallises in small prisms melting and decomposing at 252°.

*Ethyl propionylsemicarbazinopropionate* melts at 156°, and is readily soluble in water or alcohol; the corresponding *n*-butyryl compound melts at 148°, the isobutyryl derivative at 182°, the isovaleryl compound at 174°, and the chloroacetyl compound at 135°. *3-Hydroxy-5-ethyltriazole-1-propionic acid* crystallises in needles, blackens at 240°, and decomposes at 258°; it dissolves readily in alcohol and moderately in water. *3-Hydroxy-5-n-propyltriazolepropionic acid* crystallises in needles, decomposes at 249°, and is readily soluble in water; the isopropyl derivative decomposes at about 240°, and the isobutyl compound at 211°; the last substance dissolves in water with the greatest readiness.

*Ethyl benzenesulphosemicarbazinopropionate*,  
 $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{SO}_2\text{Ph}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ ,  
 crystallises from alcohol in long prisms and melts at 151°.

*Ethyl carboxyethylsemicarbazinopropionate*,  
 $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ ,  
 melts at 148°. *Ethyl 3-amino-5-diazolone-1-propionate*,



obtained from ethyl semicarbazinopropionate, carbonyl chloride, and sodium hydrogen carbonate, crystallises from water in long needles melting at 57°. *Ethyl 3-amino-5-thiodiazolone-1-propionate* crystallises in needles, melts at 117.5°, and is only sparingly soluble in water.

J. J. S.

**Compounds of Diantipyrinemethane (Formopyrine).** By GUSTAVE PATEIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 600—605. Compare Abstr., 1898, i, 493).—Formopyrine interacts with iodine in alcoholic solution to form a *tetraiodide*,  $\text{CH}_2(\text{C}_{11}\text{H}_{11}\text{ON}_2\text{I}_2)_2$ , which crystallises in slender needles possessing the colour and appearance of iodine, melts at about 135°, and is insoluble in water, but more or less soluble in organic solvents; it is decomposed by alkalis or metallic silver with the formation of formopyrine and a metallic iodide.

Formopyrine does not react with phenols directly, but when warmed with catechol in presence of sulphuric acid a *compound*,  $(\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}_4, \text{H}_2\text{O})_5[\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{SO}_3\text{H}]_4[(\text{OH})_2 \cdot \text{SO}_3\text{H} = 1:2:3]$ , is obtained which forms brilliant, nearly colourless crystals melting at 260—262°, and is decomposed by alkalis with regeneration of formopyrine. Its constitution is shown by the fact that it may also be obtained by the action of formopyrine on catechol-3-sulphonic acid. A similar and isomeric *compound* melting at 220° is obtained from resorcinol, or resorcinol-4-sulphonic acid, and formopyrine, whilst quinol yields a *compound* crystallising in colourless needles melting at 218—220°, which differs from the two preceding derivatives in containing molecular proportions of formopyrine and quinolsulphonic acids.

N. L.



**Relationship between Azoxybenzene and Diazobenzene.** By EUGEN BAMBERGER (*Ber.*, 1900, 33, 1957—1959. Compare following abstract).—The introduction of a hydroxy-group into azoxybenzene renders it possible to oxidise one ring; the product is in every case an *isodiazotate*, and no normal diazotate could be detected.

T. M. L.

**Action of Aqueous Sodium Hydroxide on Nitrosobenzene.** By EUGEN BAMBERGER (*Ber.*, 1900, 33, 1939—1957).—By the action of aqueous sodium hydroxide on nitrosobenzene at 100°, the following substances were produced: Azoxybenzene, nitrobenzene, a crystalline substance melting at 242—243°, *o*-aminophenol with a trace of *p*-aminophenol, aniline, *o*-hydroxyazobenzene, *o*-hydroxyazoxybenzene, *iso-o*-hydroxyazoxybenzene, and *p*-hydroxyazoxybenzene.

*o*-Hydroxyazobenzene,  $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot OH$ , crystallises from ether in orange-red, silky needles with a blue metallic lustre, melts at 82·5—83°, is volatile with steam, has a normal molecular weight, and in a saturated aqueous solution (7·57 mg. per litre) gives  $K_{25} = 2 \cdot 27 \times 10^{-6}$ ; the copper salt crystallises from alcohol in reddish-brown, silky needles with a slight green lustre, and melts and decomposes at 225—226°; the phenol is reduced by zinc dust and ammonium chloride to aniline and *o*-aminophenol, thus establishing its constitution.

*o*-Hydroxyazoxybenzene,  $C_6H_5 \cdot N_2O \cdot C_6H_4 \cdot OH$ , forms golden-yellow, silky, felted needles, melts at 75·5—76°, is volatile with steam, dissolves in aqueous sodium hydroxide, and less readily in hot sodium carbonate, the latter solution depositing a part of the phenol on cooling; it is oxidised by alkaline permanganate to an *isodiazot*-salt, when reduced yields aniline and *o*-aminophenol, and is converted by strong sulphuric acid into *o*-hydroxyazobenzene.

*iso-o*-Hydroxyazoxybenzene, isomeric with the preceding compound, forms minute, golden-yellow, silky needles, is volatile with steam, melts at 108—108·5°, dissolves in alkalis, is oxidised to an *isodiazot*-salt, and when reduced yields aniline and *o*-aminophenol; it has not been ascertained in what respect it differs from the preceding compound.

*p*-Hydroxyazoxybenzene crystallises from light petroleum or benzene in yellow, silky needles, melts at 156·5°, is much less readily soluble in light petroleum than the preceding compounds, and is not volatile with steam; it dissolves in alkalis, is oxidised by alkaline permanganate to an *isodiazot*-salt, and reduced to aniline and *p*-aminophenol; it can be prepared synthetically by the action of phenylhydroxylamine on *p*-nitrosophenol.

Nitrosobenzene is only very slowly acted on by aqueous sodium hydroxide in the cold; the product contains a very much larger amount of resin than in the preceding case, and very little nitrobenzene, but a considerable amount of the isomeric *p*-nitrosophenol; the four acids described above are only produced in very small quantities when the reaction takes place in the cold. T. M. L.

**Metallic Derivatives of *s*-Dibenzoylhydrazine and the Transformation of Dibenzoylhydrazine into Azodibenzoyl.** By ROBERT STOLLÉ and A. BENRATH (*Ber.*, 1900, 33, 1769—1770).—On boiling dibenzoylhydrazine for a short time with alcoholic potass-

ium hydroxide (1 mol.), the *potassium* derivative,  $N_2HKBz_2$ , separates in flat, lustrous needles, sparingly soluble in alcohol; the analogous *silver* derivative is a pale yellow powder, which is not acted on by light, and, on shaking with an ethereal solution of iodine, yields *s*-dibenzoylhydrazine along with *azodibenzoyl*,  $NBz:NBz$ . The latter crystallises in slender, orange-red needles and melts at  $117-118^\circ$ , decomposing slightly above this temperature; when boiled with alcohol, a gas is evolved, and the solution, initially coloured, becomes colourless, apparently owing to the reduction of the compound to *s*-dibenzoylhydrazine.

W. A. D.

**Diazobenzene Nitrate from Nitrosophenylhydrazine.** By LEOPOLD RÜGHEIMER (*Ber.*, 1900, 33, 1718).—When the gases obtained by the action of arsenious acid on nitric acid are passed over solid potassium nitrite into a dilute solution of nitrosophenylhydrazine in dry ether, diazobenzene nitrate separates, and can be purified by dissolving in alcohol and precipitating with ether.

T. M. L.

**Action of Acyl Cyanoacetic Esters on Benzenediazonium and Diphenyltetrazonium Chlorides.** By G. FAVREL (*Compt. rend.*, 1900, 131, 190—192).—When an ethereal acylcyanoacetate is added to a solution of benzenediazonium chloride containing excess of sodium acetate or sodium tartrate, the acyl radicle is displaced by the diazo-group, and the corresponding fatty acid is eliminated; the product is a crystalline precipitate, consisting of a mixture of the  $\alpha$ - and  $\beta$ -ethyl benzeneazocycanoacetates, the one melting at  $124-125^\circ$ , and the other at  $84-85^\circ$ . Acetic acid is set free when ethylacetocycanoacetate is employed, whilst propionic acid is eliminated from the corresponding propionyl derivative. By the action of diphenyltetrazonium chloride on the acylcyanoacetates,  $\alpha$ - and  $\beta$ -azo-compounds are similarly obtained, but in this case the reaction is complicated by secondary changes.

G. T. M.

**Action of Chloroform and Chloral Hydrate on Hæmoglobin.** By EMANUEL FORMÁNEK (*Zeit. physiol. Chem.*, 1900, 29, 416—422).—Both chloroform and chloral hydrate are good precipitants of the blood pigment, particularly at  $56^\circ$ ; although the pigment undergoes but little change, yet this method cannot be used as a means of separating it from the blood, as the other proteids are precipitated also. Bromoform acts similarly, but less vigorously. Some criticisms are added on the results obtained by Arnold, by the use of chloroform, in his preparation of neutral hæmatin.

W. D. H.

## Organic Chemistry.

**Composition of Petroleum.** By CHARLES F. MABERY (*J. Soc. Chem. Ind.*, 1900, 19, 502—508. Compare Abstr., 1897, i, 449) — *Hydrocarbons in Pennsylvanian Petroleum boiling above 216°*.—The author has isolated the following hydrocarbons from Pennsylvanian petroleum:  $C_{13}H_{30}$  [?], boiling at 225—226°;  $C_{14}H_{32}$  [?], 237—238°;  $C_{15}H_{32}$ , 256—257°;  $C_{16}H_{34}$ , 274—275°;  $C_{17}H_{36}$ , 288—289°;  $C_{18}H_{38}$ , 300—301°;  $C_{19}H_{40}$ , 316°; also members of the paraffin series containing 21, 23, 24, 25, and 26 atoms of carbon respectively. These differ essentially both in melting and boiling points from the corresponding hydrocarbons obtained by Kraftt.

**Composition of Californian Petroleum.** [With EDWARD J. HUDSON.]—In the fractions of lower boiling point obtained from various Californian petroleum, large quantities of benzene and its homologues have been met with, together with hexane, hexamethylene, a hydrocarbon  $C_7H_{14}$ , probably hexahydrotoluene;  $C_8H_{16}$ , boiling at 118—119°,  $C_9H_{18}$ , 135°;  $C_{10}H_{20}$ , 162°;  $C_{11}H_{22}$ , 196°; and  $C_{12}H_{24}$ , 216°. The composition of these hydrocarbons was established by analysis and by molecular weight determinations. The chloro-derivatives of all were prepared, analysed, and their molecular weights ascertained. From the distillates with higher boiling points, the compounds  $C_{13}H_{26}$ — $C_{19}H_{38}$ ,  $C_{21}H_{42}$ , and naphthalene have been isolated.

**Composition of Japanese Petroleum.** [With S. TAKANO.]—Petroleum from different localities vary considerably as regards specific gravity, iodine number, and percentage of nitrogen and sulphur. The amounts of benzene homologues are larger than are contained in Pennsylvanian, but smaller than are found in Californian oil. Six fractions collected between 98° and 216° give numbers corresponding with those required for the general formula  $C_nH_{2n}$ ; the fraction boiling at 216° is  $C_{12}H_{24}$ .

**Nitrogen Compounds in Californian Oil.**—Californian oils contain a relatively large amount of nitrogen (0.91—2.39 per cent.), but this cannot be accurately estimated by the Kjeldahl method. The bases have been separated by extraction with dilute sulphuric acid, and on subsequent fractional distillation gave the series of compounds  $C_{12}H_{17}N$ , boiling at 130—140°;  $C_{13}H_{19}N$ , at 197—199°;  $C_{14}H_{21}N$ , at 215—217°;  $C_{15}H_{23}N$ , at 223—225°;  $C_{16}H_{25}N$ , at 243—245°; and  $C_{17}H_{27}N$ , at 270—275°. The bases have a high specific gravity and an extremely pungent odour resembling that of nicotine; no well defined salts could be isolated, and on oxidation with chromium trioxide a small amount of acetic acid is the only product. They form additive compounds with ethyl iodide at 110°, and it is thought probable that they are tetrahydroquinoline derivatives. The number of hydrogen atoms is uncertain.

**Sulphur Compounds in Canadian Petroleum.** [With W. O. QUAYLE.]—The following compounds have been isolated, the boiling points given being under 50 mm. pressure:  $C_7H_{14}S$ , at 71—73°;  $C_8H_{16}S$ , 79—81°;  $C_9H_{18}S$ , 97—98°;  $C_{10}H_{20}S$ , 110—112°;  $C_{11}H_{22}S$ , 114—116°;  $C_{12}H_{24}S$ , 129—131°;  $C_{13}H_{26}S$ , 168—170°;  $C_{14}H_{28}S$ , 198—200°. Potass-

ium permanganate in acid or alkaline solution converts these compounds into the corresponding sulphones. J. J. S.

**Action of Finely Divided Platinum, Cobalt and Iron on Acetylene and Ethylene.** By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 131, 267—270. Compare this vol., i, 471).—Finely divided platinum has no action on pure acetylene at the ordinary temperature, but above  $150^{\circ}$  there is intumescence and the gas is partially decomposed with liberation of carbon and formation of ethylene, together with small quantities of benzene, ethane, and hydrogen.

Cobalt, free from nickel, has no action at the ordinary temperature, but above  $200^{\circ}$  the gas is almost completely decomposed by it into hydrogen, ethane, and carbon, with a small quantity of benzene and its homologues. Iron behaves similarly, but the proportion of ethane formed is much smaller, and the chief products in addition to hydrogen and carbon are olefines and benzene.

Finely divided platinum and copper have no action on ethylene below  $400^{\circ}$ , but cobalt above  $300^{\circ}$  partially decomposes it into ethane, methane, and hydrogen, together with carbon, but without any acetylene. Iron above  $350^{\circ}$  has less action but decomposes a small part of the gas into ethane, hydrogen, and carbon. C. H. B.

**Behaviour of Acetylene on Oxidation.** By A. BASCHIERI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 391—393).—On oxidising acetylene with fuming nitric acid (sp. gr. 1.52), the principal products are nitroform and carbon dioxide; besides these, a mixture of acids is obtained, partly crystallising from benzene in pale yellow needles melting at  $145$ — $150^{\circ}$ . Two neutral products are also formed: (1) a small quantity of a pale yellow oil which is heavier than water, has an aromatic odour, and boils at  $92^{\circ}$  under 15 mm. pressure; (2) a solid,  $C_6H_4O_3N_4$ , separating from ether, alcohol, water, or light petroleum in yellowish-white needles which begin to soften at  $116^{\circ}$ , melt at  $120^{\circ}$ , and when more strongly heated give off hydrogen cyanide. T. H. P.

**Action of Hydrogen Peroxide on Unsaturated Hydrocarbons.** By CHARLES F. CROSS, EDWARD J. BEVAN, and TH. HEIBERG (*Ber.*, 1900, 33, 2015—2018).—On passing acetylene into dilute aqueous hydrogen peroxide containing a small quantity of ferrous sulphate, the main product of the reaction is acetic acid, small proportions of alcohol and acetaldehyde being also formed.

On heating benzene with a dilute solution of hydrogen peroxide (2 mols.) and a small quantity of crystallised ferrous sulphate in a reflux apparatus at  $45^{\circ}$ , the products obtained were phenol, catechol, and a trace of quinol, together with a brown, amorphous product, which, on heating with potassium hydroxide at  $200^{\circ}$ , yielded mainly catechol, and also readily formed a crystalline bromo-derivative.

T. H. P.

**Nitrotri-iodoethylene and Dinitrodi-iodoethylene.** By HEINRICH BILTZ and ERICH KEDESZY (*Ber.*, 1900, 33, 2190—2196).—The compound described by Nef (*Abstr.*, 1898, i, 114) as tri-iodovinyl

nitrate is identical with nitrotri-iodoethylene (Biltz, Abstr., 1897, i, 389). It melts at  $107^{\circ}$ , and, contrary to Nef's statement, is quite stable in the dark or in diffused daylight; it is not immediately hydrolysed by alkalis, and when reduced in either alkaline or acid solution yields ammonia.

*Dinitrodi-iodoethylene*,  $C_2I_2(NO_2)_2$ , is obtained, together with nitrotri-iodoethylene, by the action of warm fuming nitric acid on tetraiodoethylene. It crystallises in yellow, monoclinic needles, melts at  $68-69^{\circ}$ , and is readily soluble in most organic solvents, with the exception of light petroleum. It is readily decomposed by potassium hydroxide solution, and even in the dark evolves iodine.

These iodo-derivatives correspond with the bromo-compounds described by Scholl and Brenneisen (Abstr., 1898, i, 345). J. J. S.

**Influence of Hydrobromic Acid on the Rate of Action of Bromine or Trimethylene.** By GABRIEL GUSTAVSON (*Compt. rend.*, 1900, 131, 273—274).—Dry bromine acts but slowly on trimethylene, but in presence of a small quantity of hydrobromic acid the hydrocarbon is rapidly absorbed, with considerable development of heat. After some time, however, this effect disappears, although the quantity of hydrobromic acid present remains the same. The active agents in promoting the absorption are compounds of bromine and hydrobromic acid of the type described by Berthelot; if 12 grams of bromine are agitated with 0.3 c.c. of hydrobromic acid of the composition  $HBr, 5H_2O$ , the liquid separates into two layers, the upper of which contains the compounds referred to, and, if separated from the lower layer, absorbs trimethylene rapidly. The function of the hydrobromic acid seems to be similar to that of aluminium chloride or bromide. Its presence has no effect on the proportion of propylene bromide amongst the products of the bromination of trimethylene. C. H. B.

**Solutions of Ferric Chloride in Organic Solvents.** By WILLIAM GEHSNER DE CONINCK (*Compt. rend.*, 1900, 131, 275—276).—When a dilute solution of ferric chloride in alcohol of  $95^{\circ}$  is exposed to sunlight, small quantities of aldehyde are formed, and, if the liquid is filtered repeatedly through animal charcoal, the whole of the iron is removed, whilst a considerable quantity of chlorine remains in solution. The small quantity of water in the alcohol seems to have considerable influence in decomposing the iron salt. A dilute solution of ferric chloride in methyl alcohol free from water is also rapidly decomposed in a similar manner when filtered through animal charcoal. Ethyl acetate and acetone behave differently; the animal charcoal removes the iron salt as a whole, and hence it would seem that it is not decomposed in solution. C. H. B.

**Action of Potassium Hydroxide on Epichlorhydrin in the Presence of Alcohols.** II. By V. ZUNINO (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 309—311. Compare Abstr., 1899, i, 410).—By the method previously given (*loc. cit.*), the following ethers of glycerol have been prepared. The *diisopropyl* ether,  $C_6H_{20}O_3$ , a pale greenish-yellow, odourless liquid, boiling at  $112-113^{\circ}$ , and having a sp. gr. 0.917 at  $15^{\circ}$ ; the *tert.butyl* ether,  $C_{11}H_{24}O_3$ , a colourless liquid with

an irritating odour, boiling at  $209-210^{\circ}$ , and having a sp. gr.  $0.921$  at  $15^{\circ}$ ; a *dicapryl* ether,  $C_{15}H_{32}O_2$ , a pale yellow liquid with an irritating odour, boiling at  $180^{\circ}$  and having a sp. gr.  $0.987$  at  $15^{\circ}$ ; *dioctyl* ether,  $C_{19}H_{40}O_2$ , a pale yellow liquid with a very disagreeable odour, boiling at  $224^{\circ}$  and having a sp. gr.  $0.990$  at  $15^{\circ}$ ; *dibenzyl* ether,  $C_{17}H_{20}O_2$ , an opalescent liquid having a faint aromatic odour, boiling at  $157-158^{\circ}$ , and having a sp. gr.  $0.918$  at  $15^{\circ}$ . T. H. P.

**Action of Bromine and Carbon Disulphide on Sodium Methylene Compounds.** By G. WENZEL (*Ber.*, 1900, 33, 2041—2043).—On adding a slight excess of bromine, dissolved in carbon disulphide, to a suspension of freshly prepared dry ethyl sodiomalonate in this medium, a compound of the composition  $C_{16}H_{22}O_8S_3$ , and the probable constitution  $S[CS \cdot CH(CO_2Et)_2]_2$ , is obtained, which separates from alcohol in almost colourless needles, melts at  $139^{\circ}$ , and is insoluble in sodium hydroxide. It dissolves in concentrated sulphuric acid, and, after many hours standing, water precipitates from the solution a colourless acid which dissolves readily in cold sodium hydroxide.

Under similar conditions, ethyl sodiocyanoacetate gives rise to a compound of the composition  $C_{12}H_{12}O_4N_2S_3$ , which crystallises from alcohol, toluene, or glacial acetic acid in yellow needles melting at  $225^{\circ}$ .

With the sodium derivatives of acetylacetone, ethyl acetoacetate, and ethyl phenylacetate, negative results were obtained.

T. H. P.

**Haloid Hydroxy-acids.** By PETR. G. MELIKOFF (*J. pr. Chem.*, 1900, [ii], 61, 554—560).—Chlorohydraerylic acid, when distilled with sulphuric acid, yields  $\alpha$ -chloroacrylic acid; its *ethyl* ester boils at  $207-208^{\circ}$ . Hypobromous acid reacts with crotonic acid (compare Abstr., 1883, 311), to form principally  $\alpha$ -bromo- $\beta$ -hydroxybutyric acid, which crystallises in monoclinic prisms melting at  $86-87^{\circ}$  and, when distilled with sulphuric acid, yields  $\alpha$ -bromocrotonic acid;  $\beta$ -bromo- $\alpha$ -hydroxybutyric acid, which is also formed in small quantity, crystallises in rhombic prisms melting at  $96-97^{\circ}$ , yields  $\beta$ -bromocrotonic acid when distilled with sulphuric acid, and forms a sodium salt, which, when heated, yields propaldehyde. The paper concludes with a summary of the facts known about the addition of hypochlorous or hypobromous acid to unsaturated acids of the type of crotonic acid; this reaction appears to follow no special rule, but stereoisomeric unsaturated acids yield corresponding stereoisomeric haloid hydroxy-acids.

R. H. P.

**Synthesis of Sorbic Acid.** By OSCAR DOEBNER (*Ber.*, 1900, 33, 2140—2142).—It has not been found possible to synthesise sorbic acid,  $CHMe:CH:CH:CH:CO_2H$ , from crotonaldehyde and acetic acid by the Perkin reaction, but a good yield of the acid is obtained when crotonaldehyde is heated with malonic acid and pyridine. C. F. B.

**Oxidation of Citric Acid and Citrates with Potassium Permanganate or with Iron.** By LUIGI SABBATANI (*Atti Accad. Sci. Torino*, 1900, 35, 678—684).—The formation of acetonedicarb-

oxylic acid by the oxidation of citric acid with cold permanganate was discovered by the author and Bergesio (Abstr., 1899, i, 733) prior to the publication of Denigès' results (this vol., i, 204). If the oxidation is carried out in hot solutions, acetone is obtained. The neutral salts of citric acid yield oxalic acid when treated with permanganate whilst the acid salts give both acetone and oxalic acid. The best yield of acetone is obtained by adding the permanganate drop by drop to a boiling solution of the acid; if excess is used, the acid or its salts are completely decomposed into water and carbon dioxide but with smaller quantities, the amount of acetone or oxalic acid formed is proportional, within limits, to the quantity of permanganate used.

Acetone is formed when Kämmerer's citrate of iron,  $\text{FeC}_6\text{H}_6\text{O}_7 \cdot \text{H}_2\text{O}$  (Abstr., 1874, 252), or a solution of citric acid containing either iron filings or a small quantity of ferric chloride, is exposed to the air.

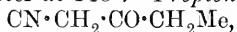
T. H. P.

**Reactions of Paraformaldehyde.** By LOUIS HENRY (*Chem. Centr.*, 1900, i, 1122—1123; from *Bull. Acad. roy. Belg.*, 1900, 48—56).—When phosphorus pentachloride acts on paraformaldehyde,  $(\text{HCHO})_n$ , at the ordinary temperature, heat is evolved and dichloromethane formed, although in rather small quantity. A good yield of dibromomethane may be obtained, however, by the action of phosphorus pentabromide or of a mixture of phosphorus trichloride (1 mol.) and bromine (1 mol.) on paraformaldehyde; in both cases, the action is rather violent. Chloromethyl acetate,  $\text{MeCO}_2 \cdot \text{CH}_2\text{Cl}$ , is best prepared by heating acetyl chloride (1 mol.) and paraformaldehyde (1 mol.) at  $100^\circ$ ; it may also be obtained by the action of chlorine, or, better, of sulphuryl chloride, on methyl acetate in sunlight. Hydrogen chloride does not act on paraformaldehyde, but by the action of hydrogen bromide, dibromomethyl ether,  $(\text{CH}_2\text{Br})_2\text{O}$ , is formed. Acetyl bromide also acts much more readily on paraformaldehyde than acetyl chloride. The product of the former reaction, *bromomethyl acetate*, is a pungent, colourless liquid, boils at  $130^\circ$  under 746 mm. and at  $70^\circ$  under 70 mm. pressure, has a sp. gr. 1.6560 at  $12^\circ$ , and does not dissolve in water but is gradually decomposed by it, forming hydrogen bromide, acetic acid, and paraformaldehyde. The formation of additive products of paraformaldehyde with acid chlorides and bromides is apparently a general reaction for the preparation of simple halogen substituted derivatives of methyl esters.

E. W. W.

**Methyl Ethyl Ketone.** By LOUIS HENRY (*Chem. Centr.*, 1900, i, 1123; from *Bull. Acad. roy. Belg.*, 1900, 57—63).—By the action of chlorine, or sulphuryl chloride, on methyl ethyl ketone in sunlight, *chloromethyl ethyl ketone*,  $\text{CH}_2\text{Cl} \cdot \text{COEt}$ , and *methyl  $\beta$ -chloroethyl ketone*,  $\text{COMe} \cdot \text{CHClMe}$ , are formed. The former boils at  $124$ — $125^\circ$ , and, by the action of nitric acid, yields chloroacetic acid, whilst the latter boils at  $114$ — $115^\circ$ , and, on oxidation, forms  *$\alpha$ -chloropropionic acid*. Bromine also attacks the ketone energetically, forming two *monobromo* derivatives, each of which boils about  $20^\circ$  higher than the corresponding chloro derivative. By the action of an alcoholic solution of potassium acetate on the chloro-ketones, the *acetates*

$\text{CH}_3\text{Ac}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$  and  $\text{COMe}\cdot\text{CHMeAc}$  are formed respectively; the former boils at  $176^\circ$ , and the latter at  $164^\circ$ . The corresponding keto-alcohols, *propionyl carbinol*,  $\text{CH}_2(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\text{Me}$ , and *methylacetyl carbinol*,  $\text{COMe}\cdot\text{CHMe}\cdot\text{OH}$ , prepared by hydrolysing the acetates, are colourless liquids, heavier than water and soluble in it; the former boils at  $160^\circ$  and the latter at  $148^\circ$ . *Propionylacetonitrile*,



prepared by the action of a cold concentrated aqueous solution of potassium cyanide on the corresponding chloro-derivative, boils at  $164\text{--}165^\circ$ .  *$\alpha$ -Acetylpropionitrile*,  $\text{CN}\cdot\text{CHMe}\cdot\text{COMe}$ , similarly obtained, boils at  $145\text{--}146^\circ$  and is insoluble in water. In both these nitriles the hydrogen atom combined with the carbon to which the cyanogen group is attached may be replaced by metals. By the action of methyl iodide on the sodium compound of  *$\alpha$ -acetylpropionitrile*, *dimethylacetylacetonitrile*,  $\text{CN}\cdot\text{CMe}_2\cdot\text{COMe}$ , boiling at  $163\text{--}164^\circ$ , is formed.  *$\alpha$ -Acetyl- $\alpha$ -chloropropionitrile*, prepared by the action of sulphuryl chloride on the ketonitrile, or on its sodium compound, is a faintly yellow liquid of an extremely pungent odour, boils at  $95^\circ$  under 45 mm. pressure and, when treated with potassium cyanide, yields *methylacetylmalonitrile*,  $\text{CMe}(\text{CN})_2\cdot\text{COMe}$ , which boils at  $122^\circ$  under 30 mm. pressure. All the cyano-derivatives are easily decomposed by acids. The ketonitriles withstand the action of aqueous solutions of alkalis much better than the isomeric butyryl and isobutyryl cyanides

E. W. W.

**Condensation of Nitromalonic Aldehyde with Ketones and Ketonic Acids.** By HENRY B. HILL, CHARLES A. SOCH, and GEORGE OENSLAGER (*Amer. Chem. J.*, 1900, 24, 1—15. Compare Abstr., 1899, i, 788).—The condensation products of sodium nitromalonaldehyde with methyl ethyl ketone, dibenzyl ketone, ethyl acetoacetate, levulic acid, and acetonedicarboxylic acid have been studied. The condensation takes place most readily in cold aqueous solution in the presence of a slight excess of sodium hydroxide, but with dibenzyl ketone it is advisable to employ an alcoholic solution.

With methyl ethyl ketone, the product is 4-nitro-*o*-cresol.

2:6-Diphenyl-4-nitrophenol, obtained from dibenzyl ketone, crystallises from hot alcohol in obliquely truncated prisms melting at  $135\text{--}136^\circ$ . The potassium derivative,  $\text{C}_{18}\text{H}_{12}\text{O}_3\text{NK}\cdot\text{H}_2\text{O}$ , crystallises in short, yellow needles sparingly soluble in cold water, and when dehydrated at  $100^\circ$  becomes a brilliant red; the methyl ether forms oblique prisms melting at  $152\text{--}153^\circ$  (corr.). The corresponding aminophenol melts at  $149\text{--}150^\circ$  (corr.), the quinone at  $135\text{--}136^\circ$  (corr.), and the quinol at  $179\text{--}180^\circ$  (corr.) (compare Borsche, this vol., i, 25).

*m*-Nitrosalicylic acid is obtained from ethyl acetoacetate.

With levulic acid, 5-nitro-2-hydroxyphenylacetic acid is formed; it crystallises from water in long, slender prisms, melts, when rapidly heated, at  $160\text{--}162^\circ$ , but if kept at  $148\text{--}149^\circ$  for 15 minutes it also melts, owing to its conversion into a lactone,  $\text{C}_8\text{H}_5\text{O}_4\text{N}$ , which sublimes in an atmosphere of carbon dioxide under a pressure of 50—60 mm., as large, colourless, transparent prisms, melts at  $187\text{--}188^\circ$  (corr.),



and dissolves readily in hot benzene, acetone, or acetic acid. The *ethyl* ester crystallises from alcohol in flat prisms melting at  $154\text{--}155^\circ$  (corr.).

2 : 6-Dicarboxy-4-nitrophenol,  $\text{OH} \cdot \text{C}_6\text{H}_2(\text{CO}_2\text{H})_2 \cdot \text{NO}_2$ , obtained from acetonedicarboxylic acid, crystallises from hot water in finely felted, colourless needles containing  $1\text{H}_2\text{O}$ . The anhydrous acid melts at  $213\text{--}214^\circ$  (corr.), and the hydrated form some  $20^\circ$  lower. The various sodium salts and the silver salt,  $\text{C}_8\text{H}_3\text{O}_7\text{Na}_2$ , have been prepared.

J. J. S.

**An Optically Inactive Pentose in Urine.** By CARL NEUBERG (*Ber.*, 1900, 33, 2243—2254. Compare Salkowski, *Abstr.*, 1893, ii, 100; 1899, ii, 679).—Salkowski's pentose has been purified by conversion into the diphenylhydrazone, and the hydrolysis of this hydrazone by Ruff and Ollendorff's method (this vol., i, 77). From a study of the derivatives, it would appear that this pentose is *r*-arabinose, and it is thus the first racemic sugar which has been found to occur naturally.

*r*-Arabinosediphenylhydrazone,  $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_4$ , crystallises from aqueous pyridine in colourless needles, sinters at  $203^\circ$ , melts at  $206^\circ$ , and is sparingly soluble in most solvents. When decomposed with formaldehyde solution, it yields a sugar identical with *r*-arabinose; the osazone melts at  $166\text{--}168^\circ$ , the *p*-bromophenylhydrazone at  $160^\circ$ , the corresponding osazone,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_4\text{Br}_2$ , at  $200\text{--}202^\circ$  (compare this vol., i, 139), the phenylbenzylhydrazone,  $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_2$ , at  $185^\circ$ , whereas the corresponding hydrazone of *l*-arabinose melts at  $170^\circ$  (*Abstr.*, 1897, i, 41), and of *d*-arabinose at  $174^\circ$  (this vol., i, 77); the phenylmethylhydrazone crystallises from alcohol in glistening needles melting at  $173^\circ$ . The sugar readily reacts with amyl mercaptan, yielding *r*-arabinose-amylmercaptal, which crystallises from 10 per cent. alcohol in glistening, felted needles melting at  $125\text{--}130^\circ$ .

The following derivatives of *l*-arabinose have been prepared:—*l*-Arabinoseamylmercaptal (compare Fischer, *Abstr.*, 1894, i, 270) melts at  $132\text{--}134^\circ$ , and 0.2 gram dissolved in 10 c.c. of hot absolute alcohol gives, in a decimetre tube, a rotation  $+0.55'$ . *l*-Arabinosediphenylhydrazone melts at  $218^\circ$ , and 0.2 gram dissolved in 4 c.c. of pyridine and 6 c.c. of absolute alcohol gives a rotation of  $+0.42'$ . J. J. S.

**Conversion of Gulonic Acid into Xylose and Galactose.** By EMIL FISCHER and OTTO RUFF (*Ber.*, 1900, 33, 2142—2147).—The calcium salt of *d*-gulonic acid, which is obtained by reduction of saccharic acid, is oxidised by hydrogen peroxide, in the presence of a little ferric acetate and in slightly warm solution, to *d*-xylose, which melts at  $141.5\text{--}143^\circ$  (corr.), has a specific rotation  $[\alpha]_D -18.6^\circ$  at  $20^\circ$ , and is oxidised by bromine to an acid of which a double salt,  $(\text{C}_5\text{H}_9\text{O}_6)_2\text{Cd} \cdot \text{CdBr}_2 \cdot 2\text{H}_2\text{O}$ , was prepared, identical in appearance and composition with the corresponding derivative of *l*-xylonic acid. Xylose can be converted into the isomeric sugar lyxose (compare *Abstr.*, 1896, i, 348). *d*-Lyxose is now found to yield *d*-galactonic acid, along with some talonic acid, when it is treated with hydrocyanic acid. Since saccharic acid is prepared from dextrose, which can be synthesised, and galactonic acid is connected with galactose and

dulcitol, the synthesis of a member of the dulcitol group, hitherto not accomplished, has now been effected.

*l*-Saccharic acid has actually been synthesised, but owing to its costliness the complete series of transformations was not carried out in this case. *l*-Gulonic acid was, however, oxidised with hydrogen peroxide, and the product was found to be identical with natural xylose (*l*-xylose). By mixing this with *d*-xylose in equal proportion and crystallising the mixture from alcohol, inactive *dl*-xylose was obtained; this melts at 129–131°, and forms a phenylosazone identical with that already obtained from xylitol (Abstr., 1894, i, 566).

C. F. B.

**Oxidation Product of Glycogen with Bromine.** By W. NIEBEL (*Zeit. physiol. Chem.*, 1900, 29, 482–485).—Chittenden (*Annalen*, 1876, 182, 206) stated that, by the oxidation of glycogen with bromine, he obtained a monobasic acid,  $C_6H_{12}O_7$ , to which the name glycogenic acid was given. In the present research, Chittenden's method with some slight modifications was found to lead, with glycogen as with other carbohydrates, to the formation of gluconic acid. The common disease of horses, hæmoglobinaemia, is believed to be due to the production of this or a higher oxidation product from the glycogen of the muscles, passing into the blood; the flesh of the horse is well known to be extremely rich in glycogen.

W. D. H.

**Sugar obtained by the Hydrolysis of Strophanthin. IV.** By FRANZ FEIST (*Ber.*, 1900, 33, 2091–2097).—Methylstrophanthobioside,  $C_{12}H_{21}O_9 \cdot OMe$ , the sugar obtained by the hydrolysis of strophanthin (Abstr., 1898, i, 329; this vol., i, 555), forms a colourless, crystalline powder melting at 207°. When hydrolysed, it yields methyl alcohol, *d*-mannose and *d*-rhamnose, and is the first crystalline methyl ether of a saccharobiose (from the combination of a hexose and a methylpentose) which has been obtained by the hydrolysis of a glucoside. R. H. P.

**Oxycelluloses and the Molecular Weight of Cellulose.** By A. NASTUKOFF (*Ber.*, 1900, 33, 2237–2243).—The author has obtained two *oxycelluloses* from cellulose, the one by the aid of bleaching powder solution and the second by means of a 1 per cent. neutral permanganate solution. Both were purified by solution in 10 per cent. sodium hydroxide solution and subsequent precipitation with hydrochloric acid, and both possess the ordinary reducing properties of oxycelluloses, yield compounds with phenylhydrazine, and turn yellow when warmed with sodium hydroxide. When the second oxycellulose is boiled with a 5 per cent. sodium hydroxide solution, 70 per cent. of it is converted into a white powder which no longer has reducing properties but possesses the same percentage composition as the original substance (compare Faber and Tollens, Abstr., 1899, ii, 854). The molecular weights of triacetylcellulose and triacetyl-oxycellulose have been determined in nitrobenzene solution by the boiling point method. The results point to a molecule  $40C_6H_{10}O_5$  for cellulose and indicate that the formation of oxycellulose by the aid of bleaching powder is merely a process of oxidation and not of hydrolysis.

J. J. S.

**Cellulose Nitrates.** By A. LUCK and CHARLES F. CROSS (*J. Soc. Chem. Ind.*, 1900, 19, 642—644).—The instability of the cellulose nitrates is not merely due to incomplete removal of all traces of the nitrating acid, as subsequent extraction with water, alcohol, ether, or benzene does not render them stable. Treatment with 50 per cent. aqueous acetone, however, renders the substance much more stable than when boiled and washed in water in the usual way, whilst with 90—93 per cent. acetone structural disintegration of the nitrate occurs, and the substance can be obtained in the form of a hard, dense powder. The impurities which lower the stability of the nitrate are present in the acetone filtrate, and seem to have acid characters, as they yield insoluble lead salts ( $\text{PbO}$ , 60—63, and N, 3.5 per cent.); their baneful influence may be eliminated by treating the nitrate with lead or zinc oxide. The purest cellulose nitrate, however, slowly decomposes with formation of unstable acid products when boiled for some time in water. J. J. S.

**Preparation and Properties of Diastase-Achroodextrin III.** By EUGEN PRIOR and D. WIEGMANN (*Zeit. angew. Chem.*, 1900, 464—469. Compare Abstr., 1897, i, 312).—Achroodextrin III, identical with Ling and Baker's "malto-dextrin- $\beta$ " (*Trans.*, 1897, 71, 508), is almost insoluble in 90 per cent. alcohol. It has the specific rotation  $[\alpha]_D$  171.1, and reducing power R 42.5. Its mol. weight, determined by the cryoscopic method, is 642, corresponding more closely with the formula  $2(\text{C}_{12}\text{H}_{20}\text{O}_{10})$  than with that proposed by Ling and Baker, namely,  $2(\text{C}_{12}\text{H}_{20}\text{O}_{10})\cdot\text{H}_2\text{O}$ , which is, however, the more probable expression. Phenylhydrazine gives no trace of crystalline osazone. Achroodextrin III is completely fermented by Logos yeast, partially by Saaz and Froberg yeasts, and not at all by *Saccharomyces apiculatus*; the fermentation appears to be direct, as no sugar can be detected if the yeast used has been freed from sugar before digestion. By the action of diastase, achroodextrin III is converted to *achroodextrin IV*, which is further hydrolysed into maltose (Ling and Baker, *loc. cit.*).

From the original starch-conversion, erythro-dextrin and achroodextrin II were also prepared in a pure state. The latter, after prolonged contact, is fermented to the extent of 3 per cent. by Saaz yeast, 14 per cent. by Froberg, and 75.4 per cent. by Logos yeast.

The low diffusibility of dextrans is offered as an explanation of the difficulty experienced in fermenting them. R. L. J.

**Ammonio-oxycobalt Thiocyanates.** By E. MASCETTI (*Zeit. anorg. Chem.*, 1900, 24, 188—190).—The blackish-green intermediate compounds obtained in the preparation of ammonio cobalt thiocyanates (Miotiti, this vol., i, 381) are oxycobaltamine thiocyanates. The salt,  $\text{Co}_2\text{O}_2(\text{NH}_3)_{10}(\text{SCN})_4$ , obtained by passing a current of air through a strongly ammoniacal solution of cobalt sulphate or thiocyanate and ammonium thiocyanate, crystallises in large, well-formed black crystals, and decomposes on exposure to air, changing to red and evolving ammonia. The salt  $\text{Co}_2\text{O}_2(\text{NH}_3)_{10}(\text{SCN})_2(\text{NO}_3)_2$ , obtained in the same manner from cobalt nitrate, separates in dirty,

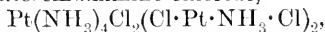
olive-green crystals, and decomposes more readily than the preceding compound.  
E. C. R.

**Preparation of Zinc Ethyl** By ARTHUR LACHMAN (*Amer. Chem. J.*, 1900, 24, 31—39. Compare Abstr., 1897, i, 461).—The author describes in fuller detail the method already given. A method is also given for the recovery of iodine from the residues obtained in the preparation of zinc ethyl.  
J. J. S.

**Pallado-oxalic Acid and Pallado-oxalates.** By H. LOISELEUR (*Compt. rend.*, 1900, 131, 262—264. Compare Vèzes, Abstr., 1899, i, 672).—*Silver pallado-oxalate*,  $\text{Ag}_2\text{Pd}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ , is almost insoluble in cold water, but crystallises from hot water in golden-yellow needles. When exposed to light or when the solution is boiled, the salt is partially reduced. The *acid*, although somewhat unstable, can be obtained in bulky, brownish-yellow needles of the composition  $\text{H}_2\text{Pd}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ ; when exposed to light, or when its solution is boiled, it decomposes into palladium, oxalic acid, and carbon dioxide. The *sodium* salt,  $\text{Na}_2\text{Pd}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , forms brownish-yellow, efflorescent needles. The *barium* salt crystallises from hot water, with  $3\text{H}_2\text{O}$ , in small yellow needles.  
C. H. B.

**Constitution of Platinum Bases.** By SOFUS M. JØRGENSEN (*Zeit. anorg. Chem.*, 1900, 24, 153—182).—Platodiammine platosemiethylene chloride,  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2(\text{Cl} \cdot \text{Pt} \cdot \text{C}_2\text{H}_4\text{Cl})_2$ , is obtained by warming sodium platinichloride with absolute alcohol until a sample of the mixture is not precipitated by concentrated ammonium chloride; the filtrate, which contains the acid corresponding to Zeise's salt, is diluted with water and a solution of platodiammine chloride added when the platodiammine salt is precipitated. It crystallises in fine yellow rhombohedra or monoclinic tablets, is very heavy, very sparingly soluble in cold water; when boiled with water or very dilute hydrochloric acid it is decomposed and yields platodiammine chloride and platinum. It can be recrystallised from hot normal hydrochloric acid in the dark; and on exposure to light is gradually converted into Magnus' salt, hydrogen platinochloride, and ethylene. *Potassium platosemiethylene chloride*,  $\text{KCl}_2\text{Pt} \cdot \text{C}_2\text{H}_4 \cdot \text{Cl} \cdot \text{H}_2\text{O}$ , crystallises in hemimorphic, monoclinic forms:  $[a:b:c = 0.6374:1:0.8637; \beta = 95^\circ 29' 5'']$ ; sp. gr. = 2.88; the *ammonium* salt is isomorphous with it  $[a:b:c = 0.6456:1:0.8690; \beta = 95^\circ 29']$ ; sp. gr. 2.68.

Platodiammine platosemiammine chloride,



described by Cossa (Abstr., 1896, ii, 251), is most easily prepared by warming platosemidiammine chloride with normal hydrochloric acid for 30—36 hours on the water-bath, and after cooling, precipitating with an aqueous solution of platodiammine chloride; it crystallises in lustrous, yellow leaflets. The potassium salt,  $\text{KCl}_2\text{Pt} \cdot \text{NH}_3 \cdot \text{Cl} \cdot \text{H}_2\text{O}$ , crystallises in the rhombic system  $[a:b:c = 0.6310:1:0.8231]$ ; the *ammonium* salt,  $\text{NH}_4\text{Cl}_2 \cdot \text{Pt} \cdot \text{NH}_3 \cdot \text{Cl} \cdot \text{H}_2\text{O}$ , forms large, lustrous, orange red prisms, and when heated with dilute ammonium chloride is converted into platosemidiammine chloride.

Potassium platosemiethylene chloride and potassium platosemiammine

chloride, when treated with silver nitrate, are converted into the corresponding silver salts, contrary to Blomstrand's and Cossa's statements.

E. C. R.

**Action of Allyl alcohol on Potassium Platinochloride.** By EINAR BILHMANN (*Ber.*, 1900, 33, 2196—2201. Compare Jørgensen, preceding abstract).—Allyl alcohol reacts with a warm aqueous solution of potassium platinochloride according to the equation  $C_3H_5 \cdot OH + K_2PtCl_4 = Cl(C_3H_5 \cdot OH)PtCl_2 \cdot ClK + KCl$ , but the *potassium platosemiallyl alcohol chloride* has not been obtained in a pure state. When the product is treated with platodiammine chloride, *platodiammine platosemiallyl alcohol chloride*,  $Pt[(NH_3)_2Cl_2Pt(C_3H_5 \cdot OH)Cl]_2$ , is obtained in the form of minute, felted, yellow needles; it is moderately soluble in cold water, but decomposes when the solution is boiled. Magnus's salt is obtained when it is boiled with hydrochloric acid, or when ammonia is added to the products of the action of allyl alcohol on potassium platinochloride, the mixture then acidified with hydrochloric acid and treated with potassium platinochloride, a dark red compound being also formed in the latter case. Alkaloidal salts give precipitates with the solution of potassium platosemiallyl alcohol chloride; the *cinchonine* compound has the composition  $C_{19}H_{22}ON_2[Cl_2Pt(C_3H_5 \cdot OH)Cl]_2$ .

J. J. S.

**Osmyloxalates.** By L. WINTREBERT (*Compt. rend.*, 1900, 131, 264—267).—Potassium osmyloxalate,  $K_2OsO_2(C_2O_4)_2 \cdot 2H_2O$ , already obtained by Vèzes by the action of oxalic acid on a solution of osmium peroxide in potassium hydroxide, can also be prepared by adding a slight excess of oxalic acid to a warm concentrated alkaline solution of potassium osmate, and crystallises in brown needles. The sodium salt is obtained in a similar manner, and forms brown needles much more soluble in cold water. Both salts are unstable in solution and gradually yield a black precipitate of osmic acid, but this change is prevented by the presence of a small quantity of oxalic acid or an alkali oxalate. The corresponding silver salt forms greenish-brown crystals and is unstable.

When potassium osmyloxalate is boiled with hydrochloric acid, it yields potassium osmichloride, chlorine, oxalic acid, and water, and hydrobromic acid yields similar results. The osmyloxalates, therefore, seem to be analogous to the osmysulphites and the salts of osmyldiammonium.

C. H. B.

**Action of a Mixture of Benzene Vapour and Hydrogen on Platinum and Palladium Black.** By GEORG LUNGE and J. AKUNOFF (*Zeit. anorg. Chem.*, 1900, 24, 191—202. Compare Harbeck and Lunge, *Abstr.*, 1898, ii, 193).—A mixture of hydrogen with 5 to 8 per cent. of benzene vapour, when passed over platinum black 25 times at the ordinary temperature, undergoes contraction corresponding with the complete conversion of the benzene into hexahydrobenzene; a complete conversion is obtained at 100° by passing the gases only three times over the platinum black. Palladium black acts in a similar manner, but more readily; the product at the ordinary temperature is, however, tetrahydrobenzene. Both platinum and palladium

black become inactive after large quantities of the gas have been passed over them, and are only rendered active again by heating in a current of hydrogen. Owing to the proximity of the boiling points, the authors were unable to separate the tetra- and hexa-hydrobenzene from the excess of benzene.

E. C. R.

**The Number of Isomeric Naphthalene Derivatives.** By HUGO KAUFFMANN (*Ber.*, 1900, **33**, 2131—2134. Compare Rey, this vol., i, 482, and Fulda, quoted by Noelting, *Mon. sci.*, 1894, [iv], **81**, 178).—A formula is given by means of which the number of isomeric naphthalene derivatives may be calculated.

C. F. B.

**Crystalline Form of Tolane.** By GIOVANNI BOERIS (*Atti Real. Accad. Lincei*, 1900, [v], **9**, i, 382—383).—Tolane crystallises in the monoclinic system [ $a:b:c=2.21081:1:1.35990$ ;  $\beta=64^{\circ}59'$ ]. The crystals show great similarity to those of stilbene, dibenzyl, and azobenzene (*Abstr.*, 1899, ii, 731 and 732).

T. H. P.

**Reactions of Aniline and of Hydroxylamine with Hydroxy- and Unsaturated Compounds.** By ALFRED TINGLE (*Amer. Chem. J.*, 1900, **24**, 45—59).—With the object of ascertaining whether  $\beta$ -ketonic esters react in the ketonic or enolic form when undergoing condensation with amino-compounds, the reaction between aniline or hydroxylamine and different hydroxy- and unsaturated esters has been studied, but so far no generalisations can be drawn.

When aniline and ethyl tartrate are boiled together for 2 hours, the products are tartranilide and *ethyl phenyltartrate*,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NHPh}$ ; the latter is soluble in water, crystallises in small, colourless plates, and melts at  $152\text{--}153^{\circ}$ .

Ethyl cinnamate and hydroxylamine yield *phenylisooxazole* (*Abstr.*, 1891, 468) and an uncrystallisable oil.

Jeanrenaud's work on the action of methyl salicylate on hydroxylamine (*Abstr.*, 1889, 870) has been repeated and his results confirmed; when, however, a smaller amount of alkali is employed, the product is salicylic acid, and not salicylhydroxamic acid.

Methyl salicylate and aniline, when perfectly dry, yield phenol and methylaniline; when the reagents are not quite dry, salicylanilide is also formed.

No reaction occurs between ethyl tartrate and hydroxylamine, ethyl cinnamate and aniline, potassium cinnamate and hydroxylamine, or sodium salicylate and aniline.

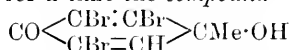
Aniline appears to react with *o*- or *p*-nitrophenol, but no well defined products have been obtained.

J. J. S.

**Removal or Substitution of Sulphonic Groups in Naphthalene Derivatives by Nascent Chlorine.** By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1900, 686—687).—Nascent bromine fails to displace sulphonic groups from naphthol- and naphthylamine-sulphonic acids. Nascent chlorine displaces sulphonic groups when they occur in *o*- and *p*-positions, except in  $\alpha$ -naphthylamine-4 : 8- and -2 : 7-disulphonic acids and  $\alpha$ -naphthol-1 : 8 disulphonic acid, but does not affect them when in the *m*-position or when heteronuclear.

R. L. J.

**Action of Nitrous Acid on Bromo- and Chloro-derivatives of Phenols.** By THEODOR ZINCKE (*J. pr. Chem.*, 1900, [ii], 61, 561—567).—Bromo- and chloro-phenols, when treated with nitrous acid, are always converted into nitrophenols, in most cases the halogen, but sometimes a hydrogen atom, being replaced by the nitro-group. In this way, mono- and di-bromo-*p*-cresol yield the same 3-bromo-5-nitro-*p*-cresol (m. p. 68°), tribromo-*p*-cresol yields a dibromonitro-*p*-cresol (m. p. 124°), and tetrabromo-*p*-cresol yields a tribromonitro-*p*-cresol (m. p. 160°); similarly, 5-bromo-*o*-cresol and 3:5-dibromo-*o*-cresol yield 3-nitro-5-bromo-*o*-cresol (m. p. 88°), tribromo-*o*-cresol yields a dibromonitro-*o*-cresol (m. p. 141°), and tetrabromo-*o*-cresol yields tribromo-3-nitro-*o*-cresol (m. p. 156°). The action of nitrous acid on bromo-derivatives of *m*-cresol is not quite clear; nitro-derivatives are produced, but molecular transformation appears also to take place. Some of the above derivatives can also be prepared by means of nitric acid, while in some cases, for example, dichloro- and dibromo-*p*-cresol, by the action of nitric acid, the unstable nitroketones are obtained; on the other hand, chloro- and bromo-*p*-cresol, when treated with nitric acid, yield nitrated oxyketones. Tribromo-*p*-cresol, when treated with nitric acid in acetic acid solution, yields the above-mentioned dibromonitro-*p*-cresol if immediately precipitated by water, but if the solution is left for a time the compound



is obtained. This forms clear, tabular crystals, melts at 128°, gives a yellow solution in sodium hydroxide, yields a crystalline *acetyl* derivative melting at 127—128°, and is reconverted into tribromo-*p*-cresol on reduction. R. H. P.

**Derivatives of 2-Methyl-1:3:4:5-Phentetrol.** By KARL KONYA (*Monatsh.*, 1900, 21, 422—432).—3-Hydroxy-5-methoxy-2-methyl-*p*-quinone-1-monoxime, obtained when methylphloroglucinol monomethyl ether is treated with potassium nitrite and acetic acid, forms flaky, violet crystals, which have a metallic lustre and explode at 194°. When reduced with stannous chloride, it is converted into 4-amino-3-hydroxy-5-methoxy-2-methylphenol hydrochloride; this crystallises in groups of colourless, slender needles, and yields a *tetracetyl* derivative of the base, which forms small, snow-white crystals melting at 178°. When oxidised with ferric chloride, the hydrochloride forms 3-hydroxy-5-methoxy-2-methyl-*p*-quinone, crystallising in small, flaky, yellowish crystals, which begin to sublime at 160° and melt at 186°. The corresponding *quinol* crystallises in small, slender, transparent needles, oxidises quickly when exposed to air, decomposes at 134°, and yields a *triacetyl* derivative melting at 174°. R. H. P.

**Monoalkyl Ethers of Phloroglucinol.** By JOSEF HERZIG and F. AIGNER (*Monatsh.*, 1900, 21, 433—445).—Phloroglucinol monomethyl ether (this vol., i, 290) is easily prepared by the reduction of *sym*-dinitroanisole and hydrolysis of the resulting *diaminounisole dihydrochloride*, which forms a colourless, crystalline mass decomposing at 220°; the *tribromo*-derivative,  $\text{OMe} \cdot \text{C}_6\text{Br}_3(\text{OH})_2$ , crystallises in long, transparent needles melting at 123°, and forms a *diacetyl* deriva

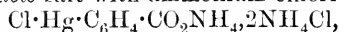
tive which crystallises in long, white needles melting at  $112-114^{\circ}$ ; the *dibenzoyl* derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OBz})_2$ , forms slender, colourless needles, melts at  $96^{\circ}$ , and is easily hydrolysed; the *diacetyl* derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OAc})_2$ , crystallises in long, colourless needles melting at  $74^{\circ}$ .

Phloroglucinol monoethyl ether can be prepared in a similar manner from *sym*-dinitrophenetole. R. H. P.

**Organo-mercury Compounds of Benzoic Acid.** By LEONE PESCI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 255—262).—*Hydroxymercuribenzoic anhydride*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{Hg} \end{smallmatrix}\rangle\text{O}$ , is prepared by heating mer-

curic acetate with benzoic acid until potassium hydroxide fails to precipitate mercuric oxide, and then treating with ammonia solution to obtain ammonium hydroxymmercuribenzoate; the anhydride is formed on treating the ammonium salt with acetic acid or the corresponding sodium salt with carbon dioxide. It forms microscopic mammillary crystals insoluble in the ordinary solvents, and is decomposed with difficulty by mineral acids; it does not melt when heated, but at high temperatures decomposes and deflagrates. The *acid* is very unstable, but its salts, formed on treating the anhydride with the corresponding hydroxide or carbonate, are strongly basic compounds readily decomposed by solvents yielding the anhydride of the acid and the metallic hydroxide; with acids, including carbonic acid, the anhydride is re-formed. The *ammonium*,  $\text{OH}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{NH}_4$ , *barium*, *calcium*, *magnesium*, *isoamylamine*, and *benzylamine* salts are described.

By the action of the halogen hydracids on hydroxymmercuribenzoic anhydride or on metallic hydroxymmercuribenzoates, chloro-, bromo-, and iodo-mercuribenzoic acids may be obtained. They are unstable substances, and in presence of the halogen hydracids tend to decompose, forming benzoic acid and the mercury haloid salt. *Chloromercuribenzoic acid*,  $\text{Cl}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , is a colourless, microcrystalline powder moderately soluble, with partial decomposition, in boiling water or methyl or ethyl alcohol. Its *sodium* salt (with  $2\frac{1}{2}\text{H}_2\text{O}$ ), *aniline* salt, and *double* salt with ammonium chloride,



are described.

*Bromomercuribenzoic acid*,  $\text{Br}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , separates from methyl or ethyl alcohol in needles; the *potassium*, *sodium* (with  $4\text{H}_2\text{O}$ ), and *barium* (with  $3\text{H}_2\text{O}$ ) salts were prepared.

*Iodommercuribenzoic acid*,  $\text{I}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , could not be obtained pure owing to the ease with which it decomposes. The *potassium*, *sodium*, and *barium* salts are described.

The author's previous work (*Abstr.*, 1894, i, 248) indicates that the mercury group in these compounds occupies the para-position relatively to the carboxyl radicle. T. H. P.

**Commercial Dichlorophthalic Acid.** By CARL GRAEBE (*Ber.*, 1900, 33, 2019—2023).—To purify commercial dichlorophthalic acid, which always contains the trichloro-acid, the following method is employed. By heating at  $180-200^{\circ}$ , the acid is completely converted into anhydride, which is then heated for about an hour in a reflux



apparatus with an equal weight of absolute alcohol; water is afterwards added until no further turbidity is formed, and the precipitated ethyl hydrogen dichlorophthalate washed with water, dried, and purified by crystallisation from carbon tetrachloride or a mixture of chloroform and light petroleum. By heating at  $200^{\circ}$ , this salt is converted into the anhydride of the acid, and on dissolving the latter in hot water, 3:6-dichlorophthalic acid (see following abstract) is obtained. It crystallises from water in well-developed, anhydrous plates, and has no definite melting point, since the formation of the anhydride begins below  $100^{\circ}$ ; the melting point of the latter is  $191^{\circ}$  (Faust gave  $187^{\circ}$ ).

*Ethyl hydrogen 3:6-dichlorophthalate*,  $C_{10}H_8O_4Cl_2$ , obtained as just described or by hydrolysing the diethyl ester with 1 mol. of potassium hydroxide, melts with incipient decomposition at  $128-130^{\circ}$ , and is readily soluble in alcohol or chloroform, but only slightly so in water.  
T. H. P.

**3:6-Dichlorophthalic Acid.** By CARL GRAEBE and S. GOUREVITZ (*Ber.*, 1900, 33, 2023—2026).—The dichlorophthalic acid of commerce, when purified by the method described in the preceding abstract, proves to be the 3:6-dichloro-acid, as is shown by its conversion into *p*-dichlorobenzene, the intermediate steps in the transformation being dichlorophthalimide, dichloroanthranilic acid, and 2:5-dichloroaniline.

*Ethyl ammonium 3:6-dichlorophthalate*,  $CO_2Et \cdot C_6H_2Cl_2 \cdot CO_2NH_4$ , is readily soluble in water and, to a less extent, in alcohol. The silver salt was prepared, and also the *diethyl* ester, which melts at  $60^{\circ}$ .

*3:6-Dichlorophthalanil*,  $C_{14}H_7O_2NCl_2$ , obtained by heating the anhydride of the acid with aniline, crystallises from alcohol in colourless needles melting at  $191^{\circ}$ .

*3:6-Dichlorophthalimide*,  $C_8H_3O_2NCl_2$ , is prepared by passing ammonia into molten dichlorophthalic anhydride, or by evaporating an ammoniacal solution of ethyl hydrogen dichlorophthalate to dryness and heating at  $240-250^{\circ}$  until gas ceases to be evolved; it is very soluble in hot alcohol, from which it crystallises in needles melting at  $242^{\circ}$ .

*3:6-Dichloroanthranilic acid*,  $C_7H_5O_2NCl_2$ , is obtained by heating an aqueous solution of dichlorophthalimide and sodium hydroxide with the calculated quantity of sodium hypobromite, and precipitating the filtered liquid with hydrochloric acid. It sublimes in colourless needles, melts at  $142^{\circ}$ , and dissolves readily in organic solvents and in hot water. It yields an unstable *hydrochloride*, but cannot be esterified by the action of hydrogen chloride and an alcohol. On treatment with sodium nitrite in alcoholic solution, the acid yields 2:5-dichlorobenzoic acid melting at  $151-153^{\circ}$  (Lellmann and Klotz gave  $153.5^{\circ}$ ), whilst when heated at  $230-240^{\circ}$  it is resolved into carbon dioxide and 2:5-dichloroaniline, from which *p*-dichlorobenzene was obtained by the diazo-reaction.  
T. H. P.

**Formation of Esters in the Phthalic Acid Group.** By CARL GRAEBE (*Ber.*, 1900, 33, 2026—2028).—Like the tetrachloro-, tetrabromo-, and tetraiodo-phthalic acids, 3:6-dichlorophthalic acid forms an exception to Victor Meyer's esterification rule, and readily

yields in the cold an alkyl hydrogen salt. This is readily explained by Meyer's assumption that in such cases, under the influence of concentrated sulphuric or hydrochloric acid, an anhydride is formed which, with the alcohol, gives rise to the alkyl hydrogen derivative. Further exceptions to the above law are afforded by 3:6-dichlorobenzoylbenzoic and tetrachlorobenzoylbenzoic acids, which are almost quantitatively esterified in the cold. It is supposed that these acids assume the tautomeric form of hydroxyphthalides, which react with the alcohol thus:  $C_6Cl_4 \left\langle \begin{array}{c} CPh(OH) \\ \text{---CO---} \end{array} \right\rangle O + Et \cdot OH = CO_2Et \cdot C_6Cl_4 \cdot CPh(OH)_2$ ; the additive compound then loses water, yielding the ethyl ester of the corresponding chlorinated benzoylbenzoic acid.

T. H. P.

**Salol.** By GEORG COHN (*J. pr. Chem.*, 1900, [ii], 61, 544—553).—Salol, when heated on a water-bath with an excess of sulphuric acid, yields a mixture of phenylsulphonic and sulphosalicylic acids. Sodium sulphosalicylate, when treated with phenol and phosphorus oxychloride, yields *diphenyl sulphosalicylate*,  $CO_2Ph \cdot C_6H_3(OH) \cdot SO_3Ph$ , which crystallises in small needles, melts at 172—173°, and gives a brown coloration with a solution of ferric chloride. *β-Dinaphthyl sulphosalicylate*, a white powder, and *diguaiacyl sulphosalicylate*, which crystallises in needles melting at 112—113°, are described.

Salol condenses with primary or secondary amines, phenol being eliminated; *salicylphenetidine* melts at 140°; *salicylanisidine* crystallises in clusters of long, slender needles melting at 159—160°, *salicyldiphenylamide* in prisms melting at 193°, and *salicylphenylhydrazide* in leaflets melting at 131°. The salicylic esters of phenols are easily obtained when salol is heated with the respective phenols. The following are described: *Salicyl Eugenol*, small prisms, melting at 73°; *β-naphthyl salicylate*, crystalline, melting at 95°; *salicylcarvacrol*, an oil; *salicyl-m-cresol*, leaflets, melting at 170°; *salicyl-p-acetaminophenol* ("salophen"), crystalline, melting at 185°; *salicyl-p-aminophenol*, needles, melting at 168—169°; *disalicyl-p-aminophenol*, melting at 176°; *monosalicylresorcinol*, melting at 137°; *salicylquinol*, slender leaflets, melting at 96—98°; *disalicylquinol*, thick leaflets, melting at 150—151°. Salol, when heated with salicylamide, yields *disalicylamide*, which crystallises in bright yellow, long needles melting at 200—203°.

Phenyl *p*-cresotate reacts with phenols in a similar manner: *β-naphthyl p-cresotate* crystallises in white leaflets melting at 103—104°, *resorcinyl di-p-cresotate* in slender needles melting at 106—107°, and *quinyl di-p-cresotate* in clusters of long needles melting at 197—198°.

Phenyl cinnamate, when treated with guaiacol, yields *cinnamylguaiacol*, which melts at 121°.

R. H. P.

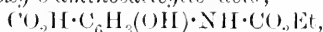
**Synthesis of *p*-Methoxyhydratropic Acid.** By J. BOUGAULT (*Compt. rend.*, 1900, 131, 270—272).—*p*-Hydroxyhydratropic acid, prepared by Trinius' method (*Abstr.*, 1885, 529), melts at 130°, and was assumed by him to be identical with phloretic acid (m. p. 128°), but this is not the case, as *p*-methoxyhydratropic acid prepared from it melts at 57°, whilst the methyl derivative of phloretic acid melts at 101°. On the other hand, the acid obtained by the action of

hydriodic acid on the methoxyhydratropic acid derived from anethole (this vol., i, 495) is identical with *p*-hydroxyhydratropic acid.

C. H. B.

***o*-Aminosalicylic Acid.** By OSKAR ZAHN (*J. pr. Chem.*, 1900, [ii], 61, 532—544).—*o*-Diazosalicylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{N}:\text{N} \end{smallmatrix}$ , obtained by diazotising *o*-aminosalicylic acid [ $\text{CO}_2\text{H}:\text{OH}:\text{NH}_2=1:2:3$ ] in glacial acetic acid solution, crystallises in lustrous, yellow needles, decomposes at  $155^\circ$ , and combines with resorcinol to form *resorcinol-o*-azosalicylic acid, a dark-red, insoluble substance which does not melt below  $300^\circ$ . The *hydrazine* obtained by the reduction of *o*-diazosalicylic acid is a very unstable substance, but condenses readily with pyruvic acid, forming the *hydrazone*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{CO}_2\text{H}$ , which melts at  $205^\circ$ .

The following derivatives of *o*-aminosalicylic acid are described: *Formyl-o*-aminosalicylic acid, grey needles decomposing at  $215^\circ$ ; *hydroxy-carboxyphenylaminocetic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , small leaflets melting at  $220^\circ$ ; the *anhydride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O}-\text{CO} \\ \diagup \diagdown \\ \text{NH}-\text{CH}_2 \end{smallmatrix}$ , small needles melting at  $174-175^\circ$ , and its *ethyl ester*, a crystalline compound decomposing at  $231^\circ$ ; *ethenyl-o*-aminosalicylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix}\text{CMe}$ , a crystalline substance melting at  $245^\circ$ ; *carbamidodisalicylic acid*,  $\text{CO}[\text{NH}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}]_2$ , microscopic crystals; *ethyl carboxy-o*-aminosalicylic acid,

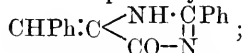


small plates melting at  $155^\circ$ , and the *anhydride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix}\text{CO}$ , a crystalline substance melting above  $300^\circ$ ; *o*-*uramidosalicylic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , a crystalline substance decomposing at  $215^\circ$ ; *phenylsulphone-o*-aminosalicylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ , small prisms melting at  $194^\circ$ ; *allylthiocarbamido-o*-salicylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_3\text{H}_5$ , small prisms melting at  $156^\circ$ ; *phenylthiocarbamido-o*-salicylic acid, crystalline clusters decomposing at  $263^\circ$ ; *benzylidene-o*-aminosalicylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}:\text{CHPh}$ , a yellowish, crystalline substance which does not melt below  $300^\circ$ ; *o*-hydroxybenzylidene-*o*-aminosalicylic acid, a yellowish substance melting at  $207^\circ$ .

R. H. P.

***α*-Amino-acids.** By EMIL ERLÉNMEYER, jun. (*Ber.*, 1900, 33, 2036—2041).—*α*-Benzoylamino-cinnamile,  $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}$ , obtained by the action of alcoholic ammonia on *α*-benzoylamino-cinnamic anhydride, crystallises from dilute alcohol in long, colourless needles melting at  $168^\circ$ . It is very stable towards mineral acids, but quickly attacked by sodium hydroxide solution, to which it imparts a yellow or yellowish-red colour. On precipitating the alkaline solution with hydrochloric acid, a small quantity of benzoylamino-cinnamic acid is formed, the principal product being, however, an intensely yellow precipitate, which crystallises from alcohol in yellow needles decomposing at  $270^\circ$ .

This *substance* is neutral and has probably the constitution



it is moderately soluble in glacial acetic acid and also in hot sodium hydroxide or carbonate solution, from which it is deposited unchanged. By prolonged boiling of a solution of the amide in acetic anhydride, it becomes reddish-yellow and part of the amide is reconverted into the anhydride, whilst if the boiling is still further continued, a pasty, red resin is formed. Boiling with quinoline converts the amide into anhydride.

The action of aniline on  $\alpha$ -benzoylaminocinnamic anhydride gives rise to the corresponding *anilide*,  $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_2$ , which crystallises in colourless needles, melts at  $238^\circ$  and dissolves in glacial acetic acid. It is very stable towards acids and alkalis, but on prolonged boiling with acetic anhydride undergoes decomposition, yielding two substances, one yellow and the other colourless.

On strongly heating piperidine with  $\alpha$ -benzoylaminocinnamic anhydride, the *piperidide* of the acid  $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$  is formed; this separates in massive, colourless crystals, melts at  $178^\circ$ , and dissolves readily in chloroform or glacial acetic acid. It strongly resists the action of acids or alkalis, and on continued heating with acetic anhydride is converted into the anhydride of the acid.

These reactions throw doubt on the view expressed by the author (*Annalen*, 1893, 275, 6; *Abstr.*, 1899, i, 759) that internal anhydrides of acids containing the group  $\cdot\text{CH:C}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$

have the constitution  $\begin{array}{c} \diagup \\ \text{CO} \end{array}$ ; thus, in the case of  $\alpha$ -benzoyl-

aminocinnamic acid the internal anhydride may be formed from the tautomeric modification of the formula  $\text{CHPh:C}(\text{CO}_2\text{H})\cdot\text{N:CPh}\cdot\text{OH}$ ,

and would then have the constitution  $\text{CHPh:C} \begin{array}{l} \text{< N} \cdot \text{CPh} \\ \text{CO-O} \end{array}$ .

T. H. P.

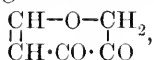
**Removal of a Sulpho-group by Reduction.** By F. J. MOORE (*Ber.*, 1900, 33, 2014—2015).—When *p*-sulphocinnamic acid is reduced by means of sodium amalgam or amalgamated aluminium, the sulphohydrocinnamic acid expected is not obtained, as the sulpho-group is split off and the resulting cinnamic acid reduced to hydrocinnamic acid.

T. H. P.

**Pyrone Group. VI. Constitution of Meconic, Comenic, and Pyromeconic Acids.** By ALBERTO PERATONER and G. LEONARDI (*Gazzetta*, 1900, 30, i, 539—565. Compare *Abstr.*, 1898, i, 69).—By the action of barium hydroxide on meconic, comenic, and pyromeconic acids, strongly reducing volatile compounds having a peculiar odour are obtained, but could not be isolated. With phenylhydrazine acetate, these products give an unstable, oily phenylhydrazone, but on heating with excess of the reagent, yield the same *phenylosazone*,  $\text{C}_6\text{H}_6(\text{N}_2\text{HPh})_3$ , which forms a straw-yellow, crystalline powder, rapidly undergoes change, and melts at  $238$ — $240^\circ$  when plunged into a previously heated bath; it dissolves slightly in benzene, but is almost insoluble in the

other organic solvents. The osazone *dibromide*,  $C_6H_6Br_2(N_2HPh)_3$ , crystallises from benzene in orange-yellow, microscopic needles melting at  $258-260^\circ$ . On hydrolysing acetylcarbinyl acetate with barium hydroxide, an unsaturated, strongly reducing, oily product is obtained which yields the same phenylosazone as that just described (compare following abstract). Hence the first product of the action of barium hydroxide on these acids is acetylcarbinol, and in presence of excess of the base 2 mols. of this alcohol condense with the elimination of  $2H_2O$  and the formation of the compound  $C_6H_8O_2$ . Quantitative study of the acids formed during the hydrolysis of the three acids shows that meconic acid yields 2 mols. of oxalic acid, comenic acid 1 mol. of oxalic acid and 1 mol. of formic acid, and pyromeconic acid 2 mols. of formic acid. In all three cases, small quantities of resinous substances are formed, besides which the acid products undergo more or less further oxidation, resulting in the formation of carbon dioxide and, especially with pyromeconic acid, small quantities of methyl alcohol.

The conclusion is drawn that meconic acid is 2:6-dicarboxy-3-hydroxy-1:4-pyronic acid (3-hydroxychelidonic acid), which confirms the suggestion of Brühl, Hjelt, and Aschan; comenic acid has the constitution  $CO_2H \cdot C \begin{smallmatrix} \diagup O-CH \\ \diagdown CH \cdot CO \end{smallmatrix} > C \cdot OH$  and pyromeconic acid



the last-named reacting also in the enolic form.

T. H. P.

**Pyrone Group. VII. A Condensation Product of Acetylcarbinol.** By ALBERTO PERATONER and G. LEONARDI (*Gazzetta*, 1900, 30, i, 565-576).—By cautious hydrolysis of acetylcarbinyl acetate, the oily *condensation product*,  $C_6H_8O_2$  (see preceding abstract), is obtained as a colourless liquid with an odour recalling that of acetophenone. It is heavier than water and boils with slight decomposition at  $185^\circ$  under the ordinary pressure, but unchanged at  $105^\circ$  under 20 mm. pressure, and does not solidify at  $-15^\circ$ . It dissolves in the organic solvents and water, is volatile in a current of steam, and reduces Fehling's solution and ammoniacal silver nitrate solution. When oxidised with permanganate or chromic acid, it yields only acetic acid. With phenylhydrazine acetate in the cold, it yields the unstable oily *phenylhydrazone* soluble in water, and, on heating, the phenylosazone, melting at  $238-240^\circ$ , described in the preceding paper. Its *semi-carbazone*,  $(C_6H_5O)N_3H_2CO$ , melts at  $190^\circ$  with previous softening at some degrees lower, and on attempting to crystallise it from alcohol an oxidation *product*,  $(C_6H_4O_3)N_3H_3CO$ , is obtained in lustrous crystals melting at  $231^\circ$ . The oily condensation product is dissolved by, but does not react with, acid chlorides. With bromine, an oily *dibromide* is obtained which evolves hydrogen bromide and resinifies on distillation. The constitution assigned to the condensation product is  $CMe \begin{smallmatrix} \diagup CH_2-O \\ \diagdown CH \cdot CO \end{smallmatrix} > CH_2$ , that of the phenylosazone (phenyltrihydrazone) being  $N_2HPh \cdot CH \cdot CMe \cdot CH \cdot C(N_2HPh) \cdot CH \cdot N_2HPh$ .

T. H. P.

**Ethyl Dimethylpyronedicarboxylate.** By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1900, 30, i, 514—525).—When reduced with either zinc and hydrochloric acid or sodium amalgam and excess of acetic acid, ethyl dimethylpyronedicarboxylate does not yield ethyl dimethyltetrahydropyronedicarboxylate (Abstr., 1896, i, 472) as would be expected, but in both cases a faintly yellow, heavy oil of the composition  $C_{13}H_{18}O_6$  (?), is obtained. It is very soluble in alcohol, ether, and other organic solvents, and is only slightly volatile in a current of steam. With ferric chloride solution, it gives an intense red coloration and in alcoholic solution instantly decolorises dilute potassium permanganate solution, but no additive compound with bromine could be prepared. Benzoyl chloride, hydroxylamine, phenylhydrazine, and semicarbazide are without action on the oil, which, with ammonia, yields a small quantity of a crystalline, nitrogenous compound melting at  $180^\circ$ . On dry distillation in a vacuum, the oil yields ethyl acetoacetate, carbon dioxide, and ethylene (?); the same products are obtained when ethyl dimethylpyronedicarboxylate itself is distilled.

By the action of semicarbazide on ethyl dimethylpyronedicarboxylate in presence of fused sodium acetate, a condensation product,  $C_{14}H_{19}O_6N_3$ , is obtained; it crystallises from alcohol in white needles which dissolve slightly in water, but readily in ether, and melt and evolve gas at  $270^\circ$ .  
T. H. P.

**Velocity of the Reaction between Sodium Hydroxide and Benzaldehyde.** By CÆSAR POMERANZ (*Monatsh.*, 1900, 21, 389—406).—The reaction between sodium hydroxide and benzaldehyde takes place in two stages (compare Kohn and Trantom, *Trans.*, 1899, 75, 1155); the first of these is the production of an additive compound,  $(Ph \cdot CHO)_2NaOH$ , which is formed by the undissociated sodium hydroxide, and is of the third order; the second is the decomposition of the additive compound into benzyl alcohol and the ions of sodium benzoate, and is of the first order.  
R. H. P.

**Action of Nitric Acid on Vanillin.** By WILLIAM B. BENTLEY (*Amer. Chem. J.*, 1900, 24, 171—181).—With 5 per cent. nitric acid at  $50^\circ$ , vanillin yields 50 per cent. of its weight of nitrovanillin along with dinitroguaiacol and an insoluble amorphous substance melting above  $390^\circ$ , which is probably identical with Tiemann's dehydrodivanillin (Abstr., 1886, 238). Nitrovanillin [ $CHO : OMe : OH : NO_2 = 1 : 3 : 4 : 5$ ] is best prepared by nitrating vanillin with fuming nitric acid in cold glacial acetic acid, and crystallises well from this solvent; it melts at  $176^\circ$ , forms an orange-yellow, efflorescent potassium salt,  $C_8H_6O_4NK \cdot 11H_2O$ , and yields dinitroguaiacol on warming with dilute nitric acid. When oxidised with slightly alkaline potassium permanganate, it gives a nitrovanillic acid which crystallises from glacial acetic acid in light yellow, efflorescent plates containing  $1\frac{1}{2}C_2H_4O_2$ , melts at  $216-216.5^\circ$ , and is probably identical with Weselsky and Benedikt's acid (Abstr., 1882, 1200).  
W. A. D.

**Nitroketones and Orthonitro-derivatives.** By ANGELO ANGELI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 41—47).—With reference to

the work of Lucas (Abstr., 1899, i, 433) and of Hantzsch (Abstr., 1899, i, 399, 401) on nitroketones, the author calls attention to the fact that, in conjunction with Rimini (Abstr., 1896, i, 295), he has obtained a compound probably belonging to that class of substances. This compound, nitropiperonylacetone,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NO}_2$ , obtained by boiling safrole nitrosite with alcohol, reacts readily with semicarbazide yielding the corresponding *semicarbazone* which crystallises from benzene in lustrous, colourless scales melting at  $151^\circ$ . Instead of the name nitroic acid given by Hantzsch (this vol., i, 89) to the parent substance from which additive compounds of nitro-derivatives with sodium hydroxide or alkylxide may be considered to be derived, the author proposes the name orthonitric acids as being more suitable.

T. H. P.

**Action of Nitrogen Tetroxide on Quinonedioximes.** By RICCARDO OLIVERT-TORTORICI (*Gazzetta*, 1900, 30, i, 526—538. Compare Abstr., 1898, i, 657).—Nitrogen peroxide first oxidises the dioximes to peroxides and then diazotises one of the NO groups, yielding unstable nitrates of nitrosodiazo-compounds, which readily give up nitrogen, forming the *p*-dinitro-derivatives of the corresponding hydrocarbons. That the primary action is one of oxidation is shown by the fact that dinitrosocymene and thymoquinonedioxime yield the same product on treatment with nitrogen peroxide.

With 1 mol. of nitrogen peroxide, benzoquinonedioxime and toluquinonedioxime both yield resinous products gradually decomposing with the formation of *p*-dinitrobenzene and *p*-dinitrotoluene respectively. With thymoquinonedioxime, which is best prepared by the action of hydroxylamine hydrochloride on nitrosocarcavrol, *nitrosodiazo-cymene nitrate*,  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_4$  [ $\text{N}_2 \cdot \text{NO}_3 : \text{Me} : \text{NO} : \text{Pr}^\beta = 1 : 3 : 4 : 6$  or  $1 : 6 : 4 : 3$ ], is obtained and forms light, canary-yellow flocks which, under the action of heat or percussion, decompose violently; on heating in a capillary tube, decomposition occurs at  $56$ – $60^\circ$ . It gives Liebermann's nitroso-reaction, and when treated in alcoholic solution with  $\beta$ -naphthol or resorcinol produces the intense red coloration characteristic of diazo-compounds. Its ethereal solution slowly decomposes, yielding *p*-dinitrocymene.

Impure naphthaquinonedioxime (containing nitrosonaphthol) and nitrogen peroxide yield *nitrosodiazonaphthalene nitrate* in the form of unstable yellow flocks which explode when heated or struck, and could not be analysed. In ethereal solution, it decomposes, giving the corresponding dinitronaphthol.

The action of nitrogen trioxide on thymoquinonedioxime and the corresponding dinitroso-compound yields the same product as is obtained when the peroxide is employed.

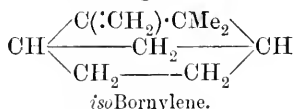
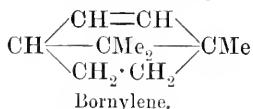
T. H. P.

**Hydroxymethylantraquinones.** By PIO MARFORI (*Chem. Centr.*, 1900, i, 1292; from *Ann. Farm. Chim.*, 1900, 85—95).—Chrysophanic acid occurs apparently in two isomeric forms which melt at  $162^\circ$  and  $171^\circ$  respectively. Isomeric acids melting at  $162^\circ$  and  $191^\circ$  respectively were also obtained by the oxidation of chrysarobin. The chrysophanic acid, prepared by passing a stream of air through a solution of chrysarobin in alcoholic potash for 6 days, crys-

tallises in golden-yellow, rhombohedral plates, melts at 162—163°, is soluble in alcohol, ether, benzene, alkalis, or sulphuric acid, but almost insoluble in cold ammonia or alkali carbonates, and insoluble in water; it is not a purgative. From the crude product of the oxidation of chrysarobin, a yellow and a red substance were also obtained by sublimation; the former melts at 160—175°, and the latter at 180—184°.

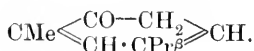
In an appendix to the original paper an oxidation product of chrysarobin melting at 162—187° is described which appears to contain several isomerides; it has a strong purgative action. Chrysarobin does not act as a purgative. E. W. W.

**Bornylene, a New Terpene.** By GEORG WAGNER and WACŁAW BRYKNER (*Ber.*, 1900, 33, 2121—2125).—By heating pinene hydriodide with potassium phenolate to 160—170°, instead of with alcoholic potash, camphene is obtained without admixture with a second hydrocarbon. This other hydrocarbon (*Abstr.*, 1900, i, 47) can be obtained in better yield than formerly by employing 40 per cent. alcoholic potash and heating in an autoclave at 170° for 4 hours. The product was fractionated, and the fraction boiling at 152—160° heated with acetic acid at 55—60° in a sealed tube, when the camphene was converted into *isobornyl* acetate, whilst the new terpene remained unattacked, and was separated by fractionation. This terpene,  $C_{10}H_{16}$ , melts at 97·5—98°, boils at 149—150° under 750 mm. pressure, and sublimes very rapidly even at the ordinary temperature; it is oxidised by dilute aqueous potassium permanganate at the ordinary temperature to camphoric acid. It is the true camphene, corresponding with camphor and borneol, and should be named *bornylene*; for the other camphene, which is oxidised by permanganate to camphenecamphoric and camphenylic acids, and camphenylene, the name *isobornylene* is proposed. The following are the constitutions assigned:



Probably bornylene has been obtained already by Spitzer (*Annalen*, 1879, 197, 129). C. F. B.

**Isocamphor.** By ENRICO RIMINI (*Gazzetta*, 1900, 30, i, 596—600. Compare Angeli and Rimini, *Abstr.*, 1897, i, 88).—To determine whether *isocamphor* contains the group  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  or  $\cdot\text{CO}\cdot\text{CHPr}^\beta\cdot$ , attempts were made to obtain condensation products of it with aldehydes, but without success. With dihydroisocamphor, however, this is possible, and on mixing it with 1 mol. of benzaldehyde and gradually adding an alcoholic solution of sodium ethoxide (1 mol.), *benzylidenedihydroisocamphor*,  $C_{10}H_{16}O\cdot\text{CHPh}$ , is obtained; it crystallises from alcohol in small, white needles melting at 217°. Hence *isocamphor* contains the group  $\cdot\text{CO}\cdot\text{CH}_2\cdot$ , and its constitution is  $\text{CMe} \begin{array}{c} \nearrow \text{CO} \text{---} \text{CH}_2 \searrow \\ \text{---} \text{CH} \cdot \text{CHPr}^\beta \end{array} \text{CH}_2$ , that of isocamphenone being



T. H. P.



**Researches in the Camphor Group.** By ENRICO RIMINI (*Gazzetta*, 1900, 30, i, 600—604).—Tanacetoneoxime, on treatment with amyl nitrite, yields crystals consisting probably of tanacetylimine nitrate. By the action of nitrous acid, it yields a *pernitroso*-derivative (compare Abstr., 1895, i, 426; 1897, i, 87, 88, 90), which decomposes on heating, evolving red vapours, and when distilled in a current of steam in presence of potassium hydroxide yields tanacetone and nitrous oxide; with hydroxylamine, tanacetoneoxime is regenerated, whilst by the action of concentrated sulphuric acid, nitrous oxide is formed, together with an oil which has a peculiar odour and is volatile in a current of steam. When treated in alcoholic solution with the calculated quantities of semicarbazide hydrochloride and sodium acetate, the pernitroso-compound gives rise to tanacetone semicarbazone, which separates in needles melting at  $178^{\circ}$ ; the same melting point is given by the carbazone when prepared directly from tanacetone, whilst this temperature is given in the literature as  $271^{\circ}$ . In a similar manner, pernitrosomenthone yields menthone semicarbazone melting at  $192$ — $193^{\circ}$ , whilst that prepared from menthone melts at  $185^{\circ}$ ; also pernitrosocamphor gives camphor semicarbazone, which is only with difficulty obtained directly from camphor. With pernitrosOfenchone, however, the action in the cold of semicarbazide acetate is similar to that of alcoholic ammonia, the product in both cases being *isopernitrosOfenchone*; when heated gently on the water-bath, however, pernitrosOfenchone and semicarbazide acetate yield *fenchone semicarbazone*,  $C_{10}H_{16}N \cdot NH \cdot CO \cdot NH_2$ , which separates from alcohol in white crystals melting at  $186$ — $187^{\circ}$ , and cannot be obtained directly.

T. H. P.

**Neroli (Orange Blossom) Oil.** By ERNST ERDMANN and HUGO ERDMANN (*Ber.*, 1900, 33, 2061—2062).—A claim for priority (see H. Walbaum, Abstr., 1899, i, 620, 621).

R. H. P.

**Origin of and Relations between the Glucosides of *Strophanthus*.** By FRANZ FEIST (*Ber.*, 1900, 33, 2063—2069. Compare Abstr., 1898, i, 328, 329).—The very variable physiological action of the pharmaceutical preparations of *Strophanthus* has been due, (1) to the indiscriminate use of different species of *Strophanthus* seeds (principally of *Strophanthus kombé* and *S. hispidus*), some of which contain no glucoside, and (2) to the existence of two glucosides, strophanthin and  $\psi$ -strophanthin, of which the latter is three or four times as strong a poison as the former.

Strophanthin has the formula  $C_{40}H_{66}O_{19}$ , and, when hydrolysed, yields strophanthidin,  $C_{27}H_{38}O_7 \cdot 2H_2O$ , and a sugar,  $C_{12}H_{21}O_9 \cdot OMe$  (see this vol., i, 540);  $\psi$ -strophanthin has the formula  $C_{30}H_{60}O_{16}$ , and, when hydrolysed, yields  $\psi$ -strophanthidin,  $C_{27}H_{37}O_5 \cdot OMe$ , and a sugar, which has not been isolated.

R. H. P.

**Strophanthin and Strophanthidin.** By FRANZ FEIST (*Ber.*, 1900, 33, 2069—2090. Compare Abstr., 1898, i, 329).—Strophanthin,  $C_{40}H_{66}O_{19} \cdot 3H_2O$ , is very hygroscopic, but when dried over sulphuric acid, becomes anhydrous and melts then at  $170^{\circ}$ ; its specific rotation

in water is  $[\alpha]_D + 10.12^\circ$ . When hydrolysed with very dilute hydrochloric acid, it yields strophanthidin,  $C_{27}H_{38}O_7$ , which crystallises with  $\frac{1}{2}H_2O$  in lustrous, monoclinic prisms  $[a:b:c = 1.1275:1:1.1179; \beta = 70^\circ 52']$ , which melts at  $169-170^\circ$ , froths at  $176^\circ$ , solidifies on cooling, and then melts at  $232^\circ$  (the melting point of the pure anhydrous substance being  $235^\circ$ ). Its specific rotation in methyl alcohol is  $[\alpha]_D + 45.45^\circ$ .

Strophanthidin, when treated with alkalis and then acidified, yields the isomeric strophanthidic lactone,  $C_{27}H_{38}O_7 \cdot \frac{1}{2}H_2O$ , which melts at  $243^\circ$ , has been previously described (*loc. cit.*) as having the formula  $(C_7H_{10}O_2)_x$ , and, when further treated with alkalis, yields anhydro-strophanthidic lactone,  $C_{27}H_{34}O_5$  (*loc. cit.*), which melts at  $345^\circ$  (corr.), and a brown acid compound,  $C_{26}H_{38}O_6$ , which melts and decomposes at  $180^\circ$ . Strophanthidin or strophanthidic lactone, when oxidised with potassium permanganate in alkaline solution, yields *strophanthic acid*,  $C_{27}H_{38}O_9$ , which crystallises in clusters melting at  $260.8^\circ$ , forms a monohydrate, which crystallises in small needles melting at  $190.7^\circ$  and an insoluble *silver* salt,  $C_{27}H_{40}O_{11}Ag_2 \cdot H_2O$ , which is derived from a dihydrate of the acid.

R. H. P.

**Chemistry of the Cell Membrane of Mosses and Liverworts.** By FRIEDRICH CZAPEK (*Chem. Centr.*, 1900, i, 1031; from *Flora*, 86, 361. Compare Abstr., 1899, i, 560).—The cell membranes of mosses and liverworts do not as a rule give the reactions of cellulose directly, but only after more or less prolonged boiling with sodium hydroxide solution. The cell walls of the mosses form an intense yellow coloration with sodium hydroxide solution, and they also, for the most part, either give Millon's reaction or produce a blackish-green coloration with salts of iron. *Sphagnum* gives Millon's reaction most distinctly, and from this moss *sphagnol* was isolated by prolonged boiling with a 1 per cent. solution of sodium hydroxide under pressure. This compound is found especially in mosses which grow in damp places, appears to be phenolic in character, gives an intense cherry-red coloration with Millon's reagent, and has rather strong antiseptic properties. The dark green iron reaction of the mosses is probably due to the presence of *dicranumtannic acid*, which may be extracted by prolonged boiling with water under pressure.

E. W. W.

**Phytochemical Studies. I. Distribution of Alkaloids in the Compositæ.** By M. GRESHOFF (*Chem. Centr.*, 1900, i, 1297; from *Ned. Tijds. Pharm.*, 12, 137—146).—A list of *Composite* which contain alkaloids is quoted. Of 150 different kinds examined, 50 were found to contain alkaloids. The fruit of *Echinops Ritro* contains 0.5 per cent. of *echinopsine*,  $C_{11}H_9ON$ , which forms rhombic crystals, melts at  $152^\circ$ , is easily soluble in chloroform, hot benzene, or hot water, and slightly so in ether. With ferric chloride, it gives a blood-red coloration. The following salts were prepared: *hydrochloride*, with  $2H_2O$ ; *sulphate*, with  $2H_2O$  and  $8H_2O$ ; *nitrate*, with  $3H_2O$ ; *oxalate*, with  $4H_2O$ ; *mercuriodide*,  $(C_{11}H_9ON, HI)_2, HgI_2$ . The poisonous action of this alkaloid is similar to that of a mixture of strychnine and brucine.

E. W. W.

**Cotarnine Cyanide as a Pseudo-salt.** By ARTHUR HANTZSCH and M. KALB (*Ber.*, 1900, 33, 2201—2208. Compare this vol., i, 115, 248).—Cotarnine cyanide, like *syn*-diazocyanides, in absolute alcoholic solution is scarcely and, even in 50 per cent. alcohol, only very slightly ionised to cotarninium cyanide, the value for  $\mu$  being only about 1/30th that of  $\mu$  for potassium cyanide under similar conditions. In aqueous solution, the conductivity is also small, but rapidly increases with rise of temperature from 0° to 40°; the temperature coefficient also rapidly increases, and is 0.1465 between 0° and 40°, whereas for a true salt it is constant, and usually about 0.02°. At higher temperatures, decomposition into the free base and hydrogen cyanide occurs.

When a few bubbles of carbon dioxide are passed into an aqueous solution of the cyanide, the colour changes to yellow and the conductivity increases considerably, probably owing to the formation of cotarninium carbonate.

Mixtures of diazonium chloride with potassium cyanide and of cotarninium chloride with potassium cyanide give constant results for their conductivities in either alcoholic or aqueous solution at 25°, whereas a mixture of cotarninium chloride with potassium cyanide in aqueous solution at 0° gives, immediately after mixing, much higher conductivities, which slowly sink to the constant value. The authors explain this phenomenon by assuming that the true cotarninium cyanide is first formed, and that this is then slowly isomerised to the non-dissociated cotarnine cyanide.

The following are given as characteristics of *pseudo*-salts: As true organic compounds, they are soluble in different organic solvents, not merely in alcohol, ether, or pyridine, but also in benzene, chloroform, or light petroleum. In solvents of the water type, and more especially in water itself, they become more or less isomerised, and at the same time ionised into the ions of the true salt, which is not stable in the solid state.

J. J. S.

**Reduction of Succinimides to Pyrrolidones.** By JULIUS TAFEL and MAX STERN (*Ber.*, 1900, 33, 2224—2236).—A 60 per cent. yield of pyrrolidone may be obtained by the electrolytic reduction of a solution of succinimide in 50 per cent. sulphuric acid.

Pyrrolidone (compare Gabriel, *Abstr.*, 1890, 360) melts at 24.65°, boils at 250.5° under 742 mm. pressure, has a sp. gr. 1.120 at 20°/4°, 1.116 at 25°/4°, 1.110 at 30°/4°, 1.097 at 40°/4°. The hydrate  $C_4H_7ON \cdot H_2O$  melts at 29.3—30.6, and solidifies at 29.7—29.9°. On the addition of nitric acid to a hot solution of pyrrolidone and phosphotungstic acid, a crystalline product is obtained. *Mercury pyrrolidone*,  $(C_4H_6ON)_2Hg \cdot H_2O$ , crystallises in colourless needles, loses its water at 100°, turns brown at 180°, and melts and decomposes at 218°. *Bromopyrrolidone*,  $C_4H_6ONBr$ , crystallises from benzene in rectangular plates, melts at 95°, is decomposed when boiled with water or treated with sodium hydroxide. *Acetylpyrrolidone*,  $C_4H_6ONAc$ , is a colourless oil distilling at 229—233°.

When pyrrolidone is boiled with alkalis, concentrated hydrochloric acid, or barium hydroxide, it is converted into  $\gamma$ -aminobutyric acid,

melting and decomposing at  $202^{\circ}$  (Gabriel gives  $184^{\circ}$ ). The acid yields a hydrochloride which is not hygroscopic (compare Schotten, Abstr., 1883, 813), an *aurichloride*, a brick-red precipitate with potassium bismuthiodide, and a *silver salt*,  $C_4H_8O_2NAg$ , soluble in warm water. The *hydrochloride* of the ethyl ester melts at  $65-72^{\circ}$ .

*isoPropylsuccinimide* is a colourless, crystalline substance melting at  $60^{\circ}$  and distilling at  $225^{\circ}$  under 743 mm. pressure. It dissolves easily in most organic solvents, is readily volatile with steam, and when electrolytically reduced yields *isopropylpyrrolidone*; this is a colourless oil which distils at  $220.5-222^{\circ}$  under 736 mm. pressure, and differs from pyrrolidone itself in its greater volatility with steam, and in not undergoing hydrolysis when boiled with barium hydroxide.

*Ethylpyrrolidone*, obtained by the electrolytic reduction of acetylpyrrolidone at temperatures below  $45^{\circ}$ , is a colourless oil distilling at  $218^{\circ}$  under 751 mm. pressure. *p-Tolylpyrrolidone*, obtained by the reduction of the corresponding succinimide in 95 per cent. sulphuric acid, crystallises from light petroleum in colourless needles melting at  $88.5^{\circ}$ , and is completely soluble in 50 per cent. sulphuric acid.

J. J. S.

**A New Trimethylpyridine.** By ICILIO GUARESCHI (*Chem. Centr.*, 1900, i, 1161; from *Atti Real. Accad. Torino*, 35).—By heating 3-cyano-4:5:6-trimethylpyridone with powdered zinc in a stream of hydrogen at a dark red heat, hydrogen cyanide is liberated, and a liquid formed which yields two fractions boiling at  $180-195^{\circ}$  and  $260-270^{\circ}$  respectively. The latter consists of 4:5:6-trimethylpyridone, which is an intermediate product of the reduction of the pyridone. The fraction of lower boiling point contains 4:5:6-trimethylpyridine; it has a pungent, pyridine-like odour, boils at  $185-188^{\circ}$ , has a sp. gr. 0.9127 at  $15^{\circ}$ , becomes yellow on exposure to air, dissolves in water forming an alkaline solution, and is easily soluble in alcohol or ether. A saturated aqueous solution becomes turbid on only very slightly warming. With copper sulphate, the aqueous solution gives a blue and with ferric chloride a brick-red precipitate. The *hydrochloride* crystallises in white, deliquescent needles, the *platinchloride* in yellow prisms melting at  $211-212^{\circ}$ , the *aurichloride* in yellow needles melting at about  $100^{\circ}$ , and the *picrate* in yellow forms. Trimethylpyridine is oxidised by potassium permanganate, forming Weidel's carbocinchomeric acid (4:5:6-pyridinetricarboxylic acid).

E. W. W.

**Action of Iodine on a Pyridine Solution of Malonic Acid.** By GIOVANNI ORTOLEVA (*Gazzetta*, 1900, 30, i, 509-514).—The action of iodine on cinnamic acid in pyridine solution gives rise to pyridine  $\beta$ -iodocinnamate (Abstr., 1899, i, 894), but by gradually adding iodine (1 mol.) to a solution of malonic acid (1 mol.) in pyridine, a *basic hydriodide* of *pyridinebetaine*,  $C_5NH_5I \cdot CH_2 \cdot CO_2H, C_5NH_5 \langle \underset{O}{\underset{||}{CH_2}} \rangle CO$ , is obtained. This compound crystallises from alcohol in massive, long white needles, which blacken at  $175-180^{\circ}$  and melt and decompose at  $250-252^{\circ}$ ; it is moderately soluble in alcohol and very soluble in water, giving an acid solution. On treatment with sodium carbonate

or silver hydroxide, pyridinebetaine is obtained, whilst sodium hydroxide solution dissolves it, giving a colourless liquid which on heating becomes brown, pyridine at the same time being set free. On reduction with sodium amalgam, or with zinc and hydrochloric acid, and neutralising with potassium hydroxide, a beautiful azure-blue coloration is produced, which disappears on shaking in the air, but reappears on standing or warming.

The formation of the pyridinebetaine compound is probably due to the decomposition of the iodomalonic acid first formed into carbon dioxide and iodoacetic acid (compare Angeli, *Abstr.*, 1893, i, 307); in presence of excess of pyridine, the iodoacetic acid acts similarly to chloroacetic acid, which yields the corresponding basic hydrochloride of pyridinebetaine (*Abstr.*, 1891, 941). T. H. P.

**Preparation of 4-Pyridinecarboxylic Acid and some of its Derivatives.** By LUDWIG TERNAJGÓ (*Monatsh.*, 1900, 21, 446—460).—Methyl *isonicotinate* is obtained to the extent of about 58 per cent. of the theoretical by heating methyl silver cinchomerionate; it crystallises in clusters of needles, and melts at  $8.5^{\circ}$ . The *hydrochloride* crystallises in large, white plates or needles decomposing at  $257^{\circ}$ , the *platinichloride* in lustrous, orange-red needles melting at  $174$ — $175^{\circ}$ , the *methiodide* in long, scarlet-red needles and prisms decomposing at  $183$ — $184^{\circ}$ . *isoNicotinic methylbetaine*,  $C_7H_7O_2N \cdot H_2O$ , obtained from the methiodide by the action of moist silver oxide, crystallises in long, lustrous needles, and its *platinichloride*, with  $H_2O$ , in long, lustrous, yellow, triclinic needles. *isoNicotinamide* crystallises in leaflets, and melts at  $155.5$ — $156^{\circ}$ . R. H. P.

**Tripyridinechromium Trichloride and Triethylenediamine Chromium Salts.** By P. PFEIFFER (*Zeit. anorg. Chem.*, 1900, 24, 279—304).—*Tripyridinechromium trichloride*,  $Cr(C_5NH_5)_3Cl_3$ , obtained by boiling anhydrous violet chromic chloride with excess of pyridine for 1 hour in a reflux apparatus, crystallises in green plates, is easily soluble in pyridine, sparingly so in methyl or ethyl alcohol, and is not attacked by cold water or ammonia. With water, the solution in pyridine gives a green precipitate, with ammonia a bright green, crystalline precipitate and reddish-violet solution, which, on addition of alcohol, yields a bluish-violet precipitate, and with silver nitrate, on warming, a precipitate of silver chloride.

*Pyridinium pentachlorochromate*,  $CrCl_5(C_5NH_6)_2 \cdot 3H_2O$ , is obtained by heating the preceding compound with concentrated hydrochloric acid, or by evaporating a solution of violet chromium chloride mixed with some chromous chloride in concentrated hydrochloric acid with pyridine hydrochloride. It crystallises in brownish-yellow, prismatic needles, is extremely deliquescent, dissolves in methyl or ethyl alcohol, and, when warmed with pyridine, is converted into tripyridinechromium trichloride; with silver nitrate, only part of the chlorine is precipitated. The corresponding *pentabromo-derivative*,  $CrBr_5(C_5NH_6)_2 \cdot 3H_2O$ , is described.

*Triethylenediaminechromium chloride*,  $Cr(C_2H_8N_2)_3Cl_3 \cdot 3\frac{1}{2}H_2O$ , is obtained by gradually adding the theoretical quantity of tripyridinechromium trichloride to ethylenediamine monohydrate. It crystallises

in orange-yellow prisms, is easily soluble in water, yielding a neutral solution, and decomposes when warmed with water or when exposed to sunlight; when treated with silver oxide, it yields a strongly alkaline solution which quickly decomposes, and gives characteristic precipitates with many metallic salts. *Triethylenediaminechromium bromide*, with  $3\text{H}_2\text{O}$  or  $5\text{H}_2\text{O}$ ; the *iodide*; the *thiocyanate*, with  $1\text{H}_2\text{O}$ ; the *nitrate*; the *dichromate*, with  $2\text{H}_2\text{O}$ ; the *sulphate*, and the *cobaltchloride* are described. *Triethylenediaminechromium hexacyanochromate*,  $\text{Cr}(\text{C}_2\text{H}_5\text{N}_2)_3\text{Cr}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ , is obtained in feathery, yellow crystals by adding potassium chromic cyanide to a concentrated solution of the chloride, and similar compounds are formed with potassium cobaltcyanide and potassium ferricyanide.

*Tripropylenediaminechromium iodide*,  $\text{Cr}(\text{C}_3\text{H}_7\text{N}_2)_3\text{I}_3 \cdot \text{H}_2\text{O}$ , obtained by adding potassium iodide to the product of the action of propylenediamine on tripyridinechromium trichloride, crystallises in small, yellow needles, and reacts with silver oxide in the same manner as the corresponding ethylenediamine salt. E. C. R.

**Formation of Indigotin from Diphenyldiketopiperazine.** By M. KUHARA and M. CHIKASHIGE (*Amer. Chem. J.*, 1900, **24**, 167—170).—When diphenyldiketopiperazine is fused with potassium hydroxide, and the product dissolved in water, indigotin is obtained probably as the result of the intermediate formation of anilinoacetic acid, and pseudindoxyl. In Flimm's synthesis of indigotin from  $\omega$ -bromoacetanilide by fusion with potash (Abstr., 1890, 383), diphenyldiketopiperazine is probably first formed, just as it is produced on boiling  $\omega$ -chloroacetanilide with alcoholic potassium hydroxide.

W. A. D.

**Oxidation [of Indigotin].** By GEORG VON GEORGIEVICS and L. SPRINGER (*Monatsh.*, 1900, **21**, 413—421).—The oxidation of indigotin by chromic acid is much accelerated by the presence of oxalic acid, and in a less degree by citric, tartaric, salicylic, benzoic, succinic, malonic, acetic, or formic acid, glycerol, or alcohol; the acceleration produced is proportional to the quantity of these substances present, or, in other words, their action is catalytic. R. H. P.

**[Crystalline Indigo-White.]** By A. BINZ and F. RUNG (*Zeit. angew. Chem.*, 1900, 412—418).—When 10 grams of indigotin, 7 grams of zinc, 60 c.c. of alcohol, 15 c.c. of water, and 1.5 grams of calcium chloride are heated for an hour in an atmosphere of carbon dioxide and the mixture cooled, indigo-white separates in minute crystals. Two other methods of preparing indigo-white in a crystalline state are described. R. L. J.

**Action of Alkyl Iodides on Indoles.** By GIUSEPPE PLANCHER (*Atti Real. Accad. Lincei*, 1900, [v], **9**, i, 115—122).—To obtain 1:3-dimethyl-3-ethyl-2-methylenindoline (Abstr., 1899, i, 452) in a pure state, methylethylacetone phenylhydrazone was condensed by heating with alcoholic zinc chloride, by which means a zincchloride,  $(\text{C}_{12}\text{H}_{15}\text{N})_2\text{ZnCl}_2$ , was obtained; it crystallises from alcohol in needles melting at  $200\text{--}202^\circ$ , and, when treated with alkali, yields 2:3-dimethyl-3-ethylindolenine, which boils at  $242\text{--}244^\circ$ , and gives a picrate

melting at 152—153° and an oxime melting at 158—159°. On digesting 2:3-dimethyl-3-ethylindolenine with methyl iodide, it is transformed into 1:3-dimethyl-3-ethyl-2-methylenindoline hydriodide, which crystallises from alcohol in needles or spangles melting and decomposing at 244°; this melting point was not obtained for the compound as prepared by any one of the three ways from indole derivatives (*loc. cit.*). The picrate melts at 123—124°, which is 10° higher than previously found. On attempting to further purify the base by hydrolysing the acetyl or benzoyl compound, impure basic products were obtained, and, in the case of the latter compound, benzoic acid and acetophenone were also formed; this confirms the constitution ascribed to the benzoyl derivatives of the methylenindolines, the stability towards permanganate being explained by their capability of existing in the tautomeric form  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CR}^1\text{R}^{11} \cdot \text{C} - \text{CH} \\ \parallel \\ \text{NMe} \cdot \text{O} \end{array} \gg \text{CPh}$ . 1:3-Dimethyl-3-ethyl-2-

methylenindoline is also formed by the condensation of methylethylacetone phenylmethylhydrazone.

[With ALDO BONAVIA.]—When ethyl isopropyl ketone phenylhydrazone is condensed by means of alcoholic zinc chloride, 3:3-dimethyl-2-ethylindolenine is formed, together with 3-methyl-2-isopropylindole, the latter boiling at 175—177° under 30 mm. and at 288—290° under 755 mm. pressure, and giving a dark, brick-coloured picrate melting at 165—166°. 3:3-Dimethyl-2-ethylindolenine crystallises from light petroleum in small, colourless prisms or scales which melt at 52—53°, boil at 129—130° under 25 mm. pressure, and are stable in air; the picrate melts at 137—138°, and the hydriodide at 186°; with nitrous acid, the base yields a ketoxime,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{N} \end{array} \gg \text{C} \cdot \text{CMe} : \text{N} \cdot \text{OH}$ , this being

the first instance among aromatic compounds of a change of this kind. With methyl iodide, the base yields 1:3:3-trimethyl-2-ethylidenindoline hydriodide, which melts at 185—186°, and is identical with the impure product obtained by Piccinini (Abstr., 1898, i, 691) by methylating 1:3:3-trimethyl-2-methylenindoline.

As just stated, 1:3:3-trimethyl-2-ethylidenindoline hydriodide melts at 186°; if, however, it is heated slowly in a test-tube, it melts at about 220°, undergoing transformation into 1:3-dimethyl-3-ethyl-2-methylenindoline,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \gg \text{CEtI} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{CMeEt} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \gg \text{CMeI} \rightarrow$

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CMeEt} \\ \diagup \quad \diagdown \\ \text{NMeI} \end{array} \gg \text{CMe}$ . This change explains the formation of 1:3-dimethyl-3-ethyl-2-methylenindoline from 2-ethyl-3-methylindole.

3-Methyl-2-isopropylindole, when treated with methyl iodide, does not yield 1:3:3-trimethyl-2-isopropylidenindoline hydriodide, but an isomeric compound (Abstr., 1899, i, 454) melting at 232°, in which the isopropyl group has probably been transferred to the 3 position. There seems to be a tendency for the heavier group to pass into the 3-position, that is, to approach the benzene nucleus.

When alkyl iodides act on 2:3-disubstituted indoles at low temperatures, the hydriodide of the corresponding indolenine is formed directly and in almost quantitative yield, the alkyl iodide being simply

added on at the double linking of the indole. Thus, on heating 2:3-dimethylindole with ethyl iodide for 6 hours at 60—85°, 2:3-dimethyl-3-ethylindolenine is obtained. This affords a much simpler method of obtaining substituted indolenines than by use of ketones.

T. H. P.

**Transformations of Tetrahydrocarbazole.** By GIUSEPPE PLANCHER (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 218—223).—[With G. TESTONI.]—The base,  $C_{14}H_{17}N$ , obtained by Zanetti and Levi (Abstr., 1895, i, 54) by the action of methyl iodide on tetrahydrocarbazole, and regarded by them as a hydroacridine derivative, must, in the light of the author's work on the methylation of indole compounds, be assumed to have the constitution  $\begin{array}{c} C_6H_4 \cdot CMe-CH_2 \\ | \\ NMe-C:CH \cdot CH_2 \end{array} > CH_2$ .

It is obtained probably in the form of a hydrate with  $1H_2O$ , melts at about 57—58°, and boils at 180—181° under 31 mm. pressure. The *picrate*,  $C_{14}H_{17}N, C_6H_3O_7N_3$ , melts at 157—158°, and the *hydriodide* at 211°, decomposing at about 225°. On heating the base with hydriodic acid and phosphorus, it loses the N-methyl group and yields a secondary base,  $C_{13}H_{15}N$ , which has an odour similar to that of thymol, gives Liebermann's nitrosoamine reaction, and readily combines with phenylcarbimide. Its *hydriodide* melts at 196—197°, and the *picrate* separates from benzene in pale yellow crystals melting at about 161°. On oxidising this base with alkaline permanganate at low temperatures, it yields a *methylcarbazolenine*,  $\begin{array}{c} C_6H_4 \cdot CMe-CH_2 \\ | \\ N=C \cdot CH_2 \cdot CH_2 \end{array} > CH_2$ , which gives a *picrate* slightly soluble in alcohol and melting at 170°. This base is also obtained, together with a non-basic indole derivative, probably methyltetrahydrocarbazole, by condensing  $\alpha$ -methylketo-hexamethylene phenylhydrazone in presence of alcoholic zinc chloride. T. H. P.

**2-Pyrrylurethane.** By ANTONIO PICCININI and L. SALMONI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 359—361).—The *hydrazide* of 2-carbopyrrolic acid,  $C_4NH_4 \cdot CO \cdot N_2H_3$ , formed by heating together the methyl ester of the acid and 50 per cent. hydrazine hydrate solution in mol. proportion, melts at 231—232°, previously becoming yellow at about 210°. It has energetic reducing properties and readily condenses with aldehydes. *Benzaldehyde pyrrolylhydrazone*,



crystallises in colourless plates melting at 164—165°. With nitrous acid, pyrrolylhydrazide is completely converted into 2-pyrroylazide,  $C_4NH_4 \cdot CO \cdot N_3$ , which is soluble in alcohol or ether and melts at 105°, evolving gas; when heated on platinum, it deflagrates slightly, and, in presence of acid, nascent hydrogen converts it into 2-carbopyrrolamide.

2-Pyrrylurethane,  $C_4NH_4 \cdot NH \cdot CO_2Et$ , obtained when 2-pyrroylazide is boiled with absolute alcohol, crystallises in long, colourless laminae or flat needles melting at 55—56°. It is a basic substance, dissolves in dilute mineral acids with more or less formation of resin, and turns



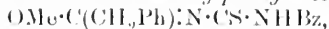
red in the air. With nitrous acid, a yellow *nitroso*-derivative,  $C_4NH_4 \cdot N(NO) \cdot CO_2Et$ , is formed, which does not melt, but decomposes at about  $200^\circ$ . In acetic anhydride, 2-pyrrolurethane dissolves in the cold without change, but on heating the solution to about  $50$ – $60^\circ$ , a crystalline *acetyl* derivative is formed together with a red compound.

T. H. P.

**Ureaimino-, Thioureaimino-, and Acylthioureaimino-esters, and Ureaamidines.** By HENRY L. WHEELER and W. MURRAY SANDERS (*J. Amer. Chem. Soc.*, 1900, 22, 365–378).—When phenylcarbimide,  $CO \cdot NPh$ , and benziminoisobutyl ester,  $OBu \cdot CPh \cdot NH$ , are allowed to react at the ordinary temperature, *phenylureaiminoisobutyl benzoate*,  $OBu \cdot CPh \cdot N \cdot CO \cdot NHPh$ , is formed. This melts at  $99$ – $100^\circ$ , reacts with aniline in warm benzene solution to form *phenylbenzenylureaphenylamidine*,  $NHPh \cdot CPh \cdot N \cdot CO \cdot NHPh$  (which melts at  $179$ – $180^\circ$  and is neutral in character), and is decomposed by hydrogen chloride, even in benzene solution, into *isobutyl chloride* and *benzoylphenylcarbamide*,  $CPhO \cdot NH \cdot CO \cdot NHPh$ . Corresponding derivatives could not be prepared from the methyl and ethyl esters and from phenylacetiminomethyl ester when the phenylcarbimide contained phosphorus oxychloride; *benzoylphenylcarbamide* and *phenylacetylphenylcarbamide*,  $CH_2Ph \cdot CO \cdot NH \cdot CO \cdot NHPh$ , were obtained at once; the latter melts at  $166^\circ$ .

Imino-esters react with phenylthiocarbimide in a similar way, but less readily, and form products which give analogous reactions. These products are less readily decomposed by hydrochloric acid, however; with ammonia, they yield phenylthiocarbimide, and form additive compounds with methyl iodide. The names, formulæ, and melting points of the substances prepared are: *Phenylthioureaiminomethyl benzoate*,  $OMe \cdot CPh \cdot N \cdot CS \cdot NHPh$ ,  $132^\circ$ , and the analogous *ethyl*,  $119^\circ$ , and *isobutyl*,  $125^\circ$ , compounds; *phenylbenzenylthioureap-anisylamidine*,  $OMe \cdot C_6H_4 \cdot NH \cdot CPh \cdot N \cdot CS \cdot NHPh$ ,  $180^\circ$ , and the analogous *phenyl*,  $151$ – $152^\circ$ , and  *$\beta$ -naphthyl*,  $182$ – $183^\circ$ , compounds.

Imino-esters also combine with acetyl and benzoylthiocarbimides,  $CS \cdot NBz$ , &c., in the same way, but even more readily; the compounds are far less stable, however. These products, as well as the amidines derived from them, form additive compounds with alkyl haloids (1 mol.); hydrochloric acid does not simply hydrolyse the alkoxy, but eliminates the alkyl benzoate, leaving benzoylthiourea, &c. Compounds prepared: *Acetylthioureaiminoisobutyl benzoate*,  $125$ – $126^\circ$ ; *Benzoylthioureaiminoisobutyl benzoate*,  $OBu \cdot CPh \cdot N \cdot CS \cdot NHBz$ ,  $120^\circ$ , and the analogous *ethyl* compound,  $131$ – $132^\circ$ ; the *methiodide*,  $204$ – $205^\circ$ , of the former, and *benzoylbenzenylthioureaphenylamidine*,  $NHPh \cdot CPh \cdot N \cdot CS \cdot NHBz$ ,  $145$ – $146^\circ$ , and the analogous *o-tolylamidine*,  $116$ – $117^\circ$ . *Benzoylthioureaiminomethylphenyl acetate*,



$116$ – $117^\circ$ , and the corresponding *ethyl* derivative,  $140$ – $141^\circ$ .

The salts of the imino-esters do not react with potassium cyanate or thiocyanate to form a carbamide or a thiocarbamide, and this seems a strong argument in support of Stieglitz's theory that the

salts in question, the hydrochloride, for instance, are not ammonium derivatives,  $\text{OR}\cdot\text{CR}^1\cdot\text{NH}_2\text{Cl}$ , but are constituted on the type  $\text{OR}\cdot\text{CR}^1\text{Cl}\cdot\text{NH}_2$ . A constitution of this type,  $\text{OBu}\cdot\text{CPh}(\text{SCN})\cdot\text{NH}_2$ , must be assigned to *benziminobutyl ester thiocyanate*, for it decomposes when warmed with water into *isobutyl benzoate* and ammonium thiocyanate, or when heated above its melting point, into *isobutyl thiocyanate* and *benzamide*. This salt is prepared by mixing cold aqueous solutions of *benziminobutyl ester hydrochloride* and *potassium thiocyanate*.

[With BAYARD BAYNES.]—Ethyl carbethoxythiocarbamate,  
 $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ ,

boils at  $135^\circ$  under 13 mm. pressure and melts at  $44^\circ$ . When heated on the steam-bath with phenylhydrazine, it yields *3-ethoxy-1-phenyl-5-triazolone*,  $\text{NPh}\begin{matrix} \text{CO}\cdot\text{NH} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{OEt} \end{matrix}$ , which melts at  $150\text{--}151^\circ$ , and is converted into Pinner's urazole (Abstr., 1887, 1043) when boiled with strong hydrochloric acid.

*Acetylphenylurethane*,  $\text{CO}_2\text{Et}\cdot\text{NPhAc}$ , was obtained by boiling phenylurethane with acetic anhydride and acetyl chloride in succession; it yields no triazole when warmed with phenylhydrazine; *acetylphenylhydrazine*, melting at  $128^\circ$ , is obtained instead. Similarly, *acetylphenylthiocarbamide* (Hugershoff, this vol., i, 156) forms no triazole with phenylhydrazine; *phenylthiocarbamide* was obtained.

C. F. B.

**Molecular Rearrangement of Thioncarbamic, Thioncarb-anilic, and Thioncarbazine Esters:  $\beta$ -Alkyl- $\alpha$ -diketotetrahydrothiazoles.** By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1900, 24, 60—82. Compare Abstr., 1899, i, 797).—It has been previously shown that when methyl thioncarbamate,  $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{OMe}$ , is treated with methyl iodide, it is transformed into the isomeric thiolcarbamate,  $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{SMe}$ . Further investigations have proved that this molecular rearrangement is characteristic of compounds of the general type  $\text{HXN}\cdot\text{CS}\cdot\text{OR}$ . Alkyl thioncarb-anilates (where  $\text{X}=\text{Ph}$ ) react less readily than the carbamates, but alkyl phenylthioncarbazines (where  $\text{X}=\text{NHPh}$ ) readily become transformed in the cold, yielding the phenylthiolcarbazines described by Busch and Stern (Abstr., 1899, i, 956).

*Ethyl phenylthioncarbazine*,  $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ , obtained together with an oily hydrazone by the action of phenylhydrazine on ethyl dithiocarbonate, crystallises from alcohol or light petroleum in needles melting at  $72\text{--}74^\circ$ , and when allowed to remain with an excess of methyl iodide, is transformed into methyl phenylthiolcarbazine, with ethyl iodide into the ethyl thiolcarbazine, and with benzyl chloride into benzyl phenylthiolcarbazine. When the thioncarbazine is treated with a 20 per cent. solution of phosgene in toluene, it is converted into *ethoxyphenylthiodiazolone*,  $\text{NPh}-\text{N} \begin{matrix} \diagup \quad \diagdown \\ \text{CO}\cdot\text{S}\cdot\text{C}\cdot\text{OEt} \end{matrix}$ , which crystallises from alcohol in colourless prisms melting at  $38^\circ$ . The sodium derivative of ethyl phenylthioncarbazine forms a yellowish-

red powder, and when either this or the free ester is treated with benzoyl chloride, *ethyl α-benzoylphenylthioncarbazinate*,  $\text{NPhBz} \cdot \text{NH} \cdot \text{CS} \cdot \text{OEt}$ , melting at  $173^\circ$  is formed. *Methyl phenylthioncarbazinate* melts at  $113^\circ$ .

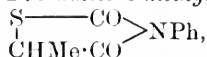
*Diethyl thiocarbonate phenylhydrazone*,  $\text{NHPh} \cdot \text{N} : \text{C}(\text{OEt}) \cdot \text{SEt}$ , obtained as a bye-product in the preparation of ethyl phenylthioncarbazinate, or by the action of alcoholic potash and ethyl iodide on this ester, is a thick, yellowish-red oil which distils at  $210\text{--}213^\circ$  under 36 mm. pressure, and on treatment with hydrogen sulphide at  $125^\circ$  for two hours, is converted back into the thion ester. When warmed for 12 hours on the water-bath with thiobenzoic acid, the products are ethyl phenylthiolcarbazinate and ethyl thiolbenzoate which distils at  $252\text{--}253^\circ$  under 760 mm. pressure. *Ethyl α-benzoylphenylthiolcarbazinate*,  $\text{NPhBz} \cdot \text{NH} \cdot \text{CO} \cdot \text{SEt}$ , obtained by treating the phenylhydrazone or ethyl phenylthiolcarbazinate with benzoyl chloride, forms lozenge-shaped crystals melting at  $138\text{--}139^\circ$ .

Methylthioncarbanilate melts at  $95\text{--}96^\circ$  (compare Orndorff and Richmond, this vol., i, 156), and when treated with methyl iodide yields methyl thiolcarbanilate (Will, Abstr., 1882, 723); *isobutyl thioncarbanilate* melts at  $77\text{--}78^\circ$  (Orndorff and Richmond,  $80\cdot5^\circ$ ), and when heated with *isobutyl iodide* does not undergo isomerisation.

When ethyl thioncarbamate and chloroacetic acid are heated together at  $100^\circ$ , the products are thioglycollic acid, ethyl thiolcarbamate, cyanuric acid, and *carbaminothioglycollic acid*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , melting at  $135\text{--}136^\circ$ . *isoAmyl thioncarbamate* and chloroacetic acid yield 2:5-diketotetrahydrothiazole, which melts at  $123\text{--}125^\circ$  and distils at  $178\cdot5\text{--}179\cdot5^\circ$  under 19 mm. pressure. The *silver* derivative, when treated with methyl iodide, yields the 1-methyl ether, melting at  $37\text{--}39^\circ$  and distilling at  $131\text{--}132^\circ$  under 15 mm. pressure.

Ethyl thioncarbanilate and chloroacetic acid yield ethyl chloride, water, and 1-phenyl-2:5-diketotetrahydrothiazole (*Annalen*, 1881, 207, 137).

[With G. K. DUSTIN.]—Ethyl-α-bromopropionate and ethyl thioncarbanilate yield 1-phenyl-2:5-diketo-3-methyltetrahydrothiazole,



crystallising in colourless needles and melting at  $103^\circ$ . Ethyl thioncarbanilate and ethyl α-bromoisobutyrate yield *ethyl carbanilo-α-thioisobutyrate*,  $\text{NHPh} \cdot \text{CO} \cdot \text{SC}(\text{CH}_3)_2 \cdot \text{CO}_2\text{Et}$ , crystallising in colourless prisms or pyramids, and melting at  $79\text{--}81^\circ$ .

[With LEEDS MITCHELL, G. K. DUSTIN, HARRY LE B. GRAY, HENRY A. NORTH and W. H. BUELL.]—α-Thiocyno-derivatives of the fatty esters are readily obtained by boiling the corresponding α-halogen fatty esters with potassium thiocyanate. They are oils with a penetrating, disagreeable odour, can be distilled under reduced pressure, and when treated with hydrochloric acid—more especially the methyl esters—undergo a transformation similar to that observed by Heintz (*Annalen*, 1865, 136, 22), and Claeson (*Ber.*, 1877, 10, 1352), yielding homologues of 2:5-diketotetrahydrothiazole. The following are the boiling points of the esters prepared:

*α*-Thiocyanoacetates: *methyl*, 120—122° (16 mm.); *ethyl*, 118—122° (15 mm.); *isoamyl*, 145—147° (17 mm.); *α*-thiocyanopropionates: *methyl*, 104—106° (15—16 mm.); *ethyl*, 107—108° (16 mm.); *isobutyl*, 130—131° (15 mm.); *isoamyl*, 141·5° (15 mm.); *α*-thiocyanoisobutyrate: *methyl*, 101—102° (17 mm.); *ethyl*, 111—115° (22 mm.); *isobutyl*, 132—133° (21 mm.); *isoamyl*, 135·5—136·5° (16 mm.); *α*-thiocyanobutyrate: *methyl*, 125° (23 mm.); *ethyl*, 134—136° (28 mm.); *isoamyl*, 158—160° (23 mm.); *α*-thiocyanoisovalerate: *methyl*, 119—121·5° (23 mm.); *ethyl*, 126—128° (19 mm.); *isobutyl*, 145—147° (19 mm.); *isoamyl*, 151—152° (14 mm.).

3-*Methyl*-2:5-diketotetrahydrothiazole, forms colourless plates melting at 46—47° and distilling at 165—168° under 20 mm. pressure. 3-*Dimethyl*-2:5-diketotetrahydrothiazole crystallises from water in extremely long, coloured prisms melting at 79—80°. 3-*Ethyl*-2:5-diketotetrahydrothiazole crystallises in six-sided prisms melting at 63—65°.

J. J. S.

**Action of Diazobenzene on Nitromethane.** By EUGEN BAMBERGER, OTTO SCHMILT, and HERBERT LEVINSTEIN (*Ber.*, 1900, 33, 2043—2061).—Diazobenzene salts have no action on nitromethane; they react with *isonitromethane* under varying conditions in two ways, (i) to form phenylazo*isonitromethane* (nitroformaldehydephenylhydrazone), which by the further action of diazobenzene may be converted into nitroformazyl or phenylnitroformaldehydephenylhydrazone and (ii) to form phenyl*isonitromethane* (phenylnitromethane), which by the further action of diazobenzene yields diphenylnitromethane or phenylazodiphenylnitromethane; in addition, phenylformazyl and benzaldehyde, benzophenonoxime and benzophenone, which are decomposition products of *isonitro*-compounds, two undetermined neutral compounds melting respectively at 105—106° and at 132° and an undetermined basic compound melting at 145° were isolated from the products of the reaction.

R. H. P.

**Formation of a Nitrosoamine by the Action of Nitrous Acid on a Primary Aromatic Amine.** By ERNST TÄUBER and FRANZ WALDER (*Ber.*, 1900, 33, 2116—2118).—When, in the preparation of Bismarck brown, a cooled solution of sodium nitrite (1 mol.) is rapidly added to a cooled solution of *m*-phenylenediamine (1 mol.) in hydrochloric acid (2 mols.), as much as 20 per cent. of the diamine can be obtained in the form of a nitroso-derivative. *Nitroso-m-phenylenediamine* crystallises in red, monoclinic plates or needles, and its hydrochloride in reddish-brown to black needles. It melts and decomposes at 210°, is reduced in acid solution to 1:2:4-triaminobenzene, yields ammonia and a nitrosoaminophenol when boiled with aqueous sodium hydroxide, and does not give Liebermann's nitrosoamine reaction.

C. F. B.

**Diazonium Hydroxides and Diazohydroxides.** By ADALBERT ENGLER and ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2147—2158. Compare Davidson and Hantzsch, *Abstr.*, 1899, ii, 6).—Many of the diazonium hydroxides are very strong bases. The dissociation constants were determined from the conductivity at 0° of dilute mixtures of the diazonium chloride with pure sodium hydroxide in molecular proportion. Anisole diazonium

hydroxide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{OH}$ , and pseudocumenediazonium hydroxide  $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{N}_2 \cdot \text{OH}$ , are bases equal in strength to the alkali hydroxides and the dissociation constants were too great to be determined. *p*-Bromobenzenediazonium hydroxide  $K$  0.0149, 2:4-dibromobenzenediazonium hydroxide  $K$  0.0136, and 2:4:6-tribromobenzenediazonium hydroxide  $K$  0.0014, the strength of the base diminishing as the number of negative radicles increases. The undissociated part does not consist of true diazonium hydroxide, but of the *syndiazohydroxide* which forms the "pseudo-base," although no time-change can here be observed. Since *p*-bromobenzenediazonium hydroxide is much less dissociated than benzenediazonium hydroxide, its solution should contain more of the *syndiazohydroxide*, and it has been found that the conversion into a *syndiazotate* is virtually complete in presence of  $2\frac{1}{2}$  mols. of sodium hydroxide, whereas benzenediazonium hydroxide requires a large excess of alkali. *p*-Nitrobenzenediazonium hydroxide is too unstable for accurate conductivity measurements, but was found to be a stronger base than ammonia.

The normal (*syn*) diazohydroxides are converted immediately into diazonium chlorides on adding 1 mol. of hydrochloric acid and no 'gradual neutralisation' phenomena could be detected by means of conductivity measurements even at  $0^\circ$  in the case of *p*-bromobenzenediazohydroxide. 'Gradual neutralisation' occurs, however, in the case of the *isodiazo*hydroxides, which exist chiefly in the form of nitrosoamines as pseudo-bases, and the conductivity of a mixture of *p*-nitrophenylnitrosoamine and hydrochloric acid only became constant after about  $3\frac{1}{2}$  hours at  $0^\circ$ .

T. M. L.

*synDiazotates*. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2158—2161).—On adding a solution of anisodiazonium bromide to 10 mols. of potassium hydroxide dissolved in an equal weight of water and cooled to  $-10^\circ$ , *potassium anisolesyndiazotate*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{OK}$ , separates as a mass of colourless flakes, which liquefies immediately in moist air, dissolves unchanged in water at  $0^\circ$ , decomposes in solution at the ordinary temperature, but can be crystallised unchanged from concentrated potassium hydroxide solution.

*Potassium pseudocumenesyndiazotate*,  $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{N}_2 \cdot \text{OK}$ , was prepared in a similar manner, but was found to be much less stable.

T. M. L.

*synDiazocyanides and Diazonium Cyanides*. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2161—2179).—The diazocyanides resemble the hydroxides (Engler and Hantzsch, this vol., i, 566) in that the dissociated portion is in the form of a diazonium cyanide,  $\text{R} \cdot \text{N}(\text{CN}) \cdot \text{N}$ , a true salt closely resembling potassium cyanide, whilst the undissociated portion is a 'pseudo-salt,'  $\text{R} \cdot \text{N} \cdot \text{N} \cdot \text{CN}$ , resembling the azo-compounds.

*Anisolesyndiazocyanide*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{CN}$ , is precipitated by alcoholic potassium cyanide from a cold solution of the diazonium chloride as an orange-red powder melting at  $50$ — $51^\circ$ , and passes in about 30 hours into the *antidiazocyanide*, which crystallises from light petroleum in brownish-red needles, melts at  $121$ — $122^\circ$ , and neither condenses with  $\beta$  naphthol nor liberates nitrogen in contact

with copper powder. The *syndiazocyanide* dissolves unchanged in alcohol to a strongly-coloured, non-conducting solution; the aqueous solution, however, consists chiefly of *anisolediazonium cyanide*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CN})\text{:N}$ , is only slightly coloured, and has  $\mu_{256}$  49.6,  $\mu_{512}$  53.9.

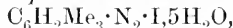
*Pseudocumenediazocyanide*, like the preceding compound, is a 'pseudo-salt' resembling the azo-compounds when in the solid state or in alcoholic solution, but in aqueous solution consists chiefly of *pseudocumenediazonium cyanide*, which gives  $\mu_{512}$  50.6 at  $0^\circ$ , and is a true salt like the diazonium chloride.

2:4-Dibromobenzenediazocyanide, unlike the two preceding compounds, is only very slightly dissociated in dilute aqueous solution. Tribromobenzenes*syndiazocyanide* shows no tendency to form a diazonium cyanide, is indifferent to hydrochloric acid, but immediately precipitates silver cyanide from alcoholic silver nitrate. *p*-Bromobenzenediazocyanide in aqueous solution is about half dissociated to the diazonium cyanide, whilst solutions of *p*-chlorobenzenediazocyanide conduct somewhat less; diazobenzene cyanide itself is rather more than half dissociated to the diazonium cyanide. T. M. L.

*anti*Diazonaphthalene Salts and Naphthylnitrosoamine. By ADALBERT ENGLER (*Ber.*, 1900, 33, 2188—2190).—Sodium *antidiazonaphthalene*,  $\text{C}_{10}\text{H}_7\cdot\text{N}\text{:N}\cdot\text{ONa}\cdot\text{H}_2\text{O}$ , rapidly turns brown, dissolves in water to a colourless solution, has  $\mu_{32}$  34.4,  $\mu_{1024}$  38.0, and thus is not appreciably hydrolysed; it is therefore a salt of a true acid. On adding acetic acid, however, the compound which is liberated is not acid to litmus, only very slightly soluble in water, and a non-electrolyte; it is therefore regarded as the 'pseudo-acid' *naphthyl-nitrosoamine*,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NO}$ , and this view is confirmed by the fact that when dissolved in benzene it does not interact with phosphorus pentachloride, acetyl chloride, or ammonia. T. M. L.

**Nature of the Diazohaloids.** By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2179—2188).—Except in certain cases where the diazonium ion is coloured, the coloured explosive diazohaloids are regarded as consisting chiefly of the true azo-compound  $\text{R}\cdot\text{N}\text{:N}\cdot\text{NCl}$ , whilst the colourless diazohaloids, which are much less explosive, are regarded as diazonium haloids,  $\text{R}\cdot\text{NCl}\text{:N}$ ; coloured nitrates and sulphates only occur when the diazonium ion is coloured.

*Mesitylenediazoidide*,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{N}_2\cdot\text{I} + 6$  or  $7\text{H}_2\text{O}$ , crystallising in golden-yellow needles, and *pseudocumenediazoidide*,



remain constant in weight at  $-5^\circ$ , effloresce at  $0^\circ$ , and then decompose. *Anisole diazoidide*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{I}$ , forms golden-yellow needles, and is somewhat more stable than the preceding compounds, but explodes when rubbed.

The remaining diazoidides in which the diazonium hydroxide is a weaker base (see Engler and Hantzsch, this vol., i, 566) are much less stable and could not be isolated.

† All the diazochlorides are colourless and not more explosive than the colourless nitrates; the yellow colour of naphthalenediazochloride is perhaps due to decomposition products. The diazobromides are

almost all coloured and explosive; pseudocumenediazobromide, at the moment of precipitation, and *p*-thiocyanobenzene diazobromide,  $\text{SCN} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Br}$ , are colourless; anisodiazobromide has only a slight greenish-yellow tint. The diaziodides are still more coloured and explosive, whilst the diazothiocyantes are intermediate between the bromides and iodides. The diazoeyanides (see this vol., i, 567) form the other limiting case, and are exclusively azo-compounds when in the solid state.

T. M. L.

**Hydrazones and Osazones from *p*-Nitrophenylhydrazine.** By FRANZ FEIST (*Ber.*, 1900, 33, 2098—2099).—*Furfuraldehyde-p-nitrophenylhydrazone* is a bright red substance which crystallises from alcohol, melts at  $127^\circ$ , and dissolves in sodium hydroxide, forming a reddish-violet solution. *1-Methylfurfuraldehyde-p-nitrophenylhydrazone* is a ruby-red powder which melts at  $130^\circ$  and dissolves in dilute sodium hydroxide, forming a cherry-red solution. *Lævulinic acid p-nitrophenylhydrazone* crystallises in small, lustrous needles which melt at  $174$ — $175^\circ$  and dissolves in sodium hydroxide, forming a deep red solution. *p-Nitrophenylrhamnosazone* crystallises in microscopic, vermilion-coloured needles which melt and froth at  $208^\circ$  and dissolve in sodium hydroxide, forming a deep blue solution.

R. H. P.

**Action of Chloroacetic Acid and Chloroacetone on Thio-carbanilides and Thiosemicarbazides.** By REINHOLD VON WALTHER and A. STENZ (*J. pr. Chem.*, 1900, [ii], 61, 575—576).—Thiocarbanilide reacts with *p*-toluidine to form phenyl-*p*-tolylthiocarbamide; if the reaction takes place in alcoholic solution, the product melts at  $158^\circ$ , but if in glacial acetic acid solution it melts at  $141^\circ$ , and is convertible into the isomeride melting at  $158^\circ$ . Phenyl-*p*-tolylthiosemicarbazide has been obtained in two forms, which melt respectively at  $165^\circ$  and  $176^\circ$ , and phenyl-*p*-tolylthiohydantoin has also been obtained in two forms, which melt at  $169^\circ$  and  $113^\circ$ . Chloroacetic acid reacts with diphenylthiosemicarbazide (m. p.  $165^\circ$ ), forming two isomeric compounds, of which one melts at  $200^\circ$  and by the action of alcoholic hydrochloric acid can be converted in the second melting at  $210^\circ$ ; phenyl-*p*-tolylthiocarbamide reacts with chloroacetone to form two thiazolines melting at  $116^\circ$  and  $136^\circ$  respectively. This isomerism is not yet explained.

R. H. P.

**Coloured Rosaniline Bases and their Colouring Properties.** By GEORG VON GEORGIEVICS (*Monatsh.*, 1900, 21, 407—412).—A continuation of the controversy between the author and Weil (compare Abstr., 1896, i, 565). The red colour which the carbinol base gradually assumes and the coloration on filter paper produced by an ethereal solution of rosaniline can be explained by the formation of a "rosaniline rosanilate" by the combination of the rosaniline ammonium base (rosanilinium, compare Hantzsch and Osswald, this vol., i, 256) with the carbinol base, which acts as an acid in the presence of strong bases.

R. H. P.

**Preparation of Phosphoryl Derivatives of Aromatic Amines.** By WILHELM AUTENRIETH and P. RUDOLPH (*Ber.*, 1900, **33**, 2099—2111).—The amine  $\text{NH}_2\text{R}$  is emulsified by shaking with slightly more than the calculated quantity of 10—25 per cent. aqueous sodium hydroxide, or 30—40 per cent. aqueous sodium carbonate, and about three times the theoretical amount of phosphorus oxychloride is added, the shaking being continued and the mixture kept cool with ice. The substituted amide,  $\text{PO}(\text{NHR})_3$ , separates; in solution, there remains a substituted amino-acid,  $\text{OH}\cdot\text{PO}(\text{NHR})_2$ , which can be precipitated by the addition of a dilute mineral acid. The phosphoramides crystallise well; they can be brominated and nitrated; they are stable in cold water and aqueous acids and alkalis, and even in boiling alcoholic potash, but are hydrolysed when heated with strong hydrochloric acid under pressure. The aminophosphoric acids are less easy to obtain crystalline, and are rather less stable; when their dry sodium salts are rubbed with phosphorus pentachloride, the chlorides,  $\text{Cl}\cdot\text{PO}(\text{NHR})_2$ , are formed; these are crystalline and stable in cold water.

The amines experimented with were aniline, *o*- and *p*-toluidine, *p*-chloroaniline, and *p*-phenetidine. Of the compounds obtained those which are new are enumerated below, with their melting points. Dianilinoorthophosphoric acid, 214—216°; *dianilinophosphoryl chloride*,  $\text{Cl}\cdot\text{PO}(\text{NHPh})_2$ , 159°. *Phosphorylbromotoluidide*,  $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{MeBr})_3$ , 222°; *di-p-toluinophosphoric acid*, 195° (not 124°; compare Rudert, *Abstr.*, 1893, i, 324). *Phosphoryl-p-chloroanilide*,  $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl})_3$ , 248—250°; *di-p-chloroanilinophosphoric acid*,  $\text{OH}\cdot\text{P}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl})_2$ , 218°. *Phosphoryl-p-phenetidine*,  $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_3$ , 168°; *nitro-derivative*,  $\text{PO}[\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{OEt}]_3$ , yellow, 126°; *di-p-phenetidino-phosphoric acid*,  $\text{OH}\cdot\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , 202°.

[W. AUTENRIETH and O. HILDEBRAND.]—Phenylmercaptan can be converted into phosphate by treatment in alkaline solution with phosphorus oxychloride, just as the phenols can. The product, phenyl trithiophosphate,  $\text{PO}(\text{SPh})_3$ , melts at 114° (not 72°).

C. F. B.

**Action of Phosphorus Thiochloride on Aromatic Amines in the Presence of Alkali.** By WILHELM AUTENRIETH and P. RUDOLPH (*Ber.*, 1900, **33**, 2112—2115).—The action of phosphorus thiochloride is similar to that of the oxychloride (preceding abstract), except that the amide is here always the main product of the reaction, and the amino-acids are less stable, and in consequence were not isolated in the pure state. A 10 per cent. sodium hydroxide solution was used, and the phosphorus thiochloride was employed in about twice the calculated amount.

The following are the new compounds prepared, with their melting points. *Thiophosphorylanilide*,  $\text{PS}(\text{NHPh})_3$ , 153—154°, identical with the supposed  $\text{PS}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_3$  of Knop (*Abstr.*, 1888, 265), but not with the probably impure compound of Chevrier (*Zeit. Chem.*, 11, 539). *Thiophosphoryl-p-phenetidine*,  $\text{PS}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_3$ , 152°. Thiophosphoryl-*p*-toluidide was also prepared.

C. F. B.



**Metallic Derivatives of Diazoaminobenzene.** By LOUIS MEUNIER (*Compt. rend.*, 1900, 131, 50—53).—The cuprous derivative of diazoaminobenzene is conveniently prepared, either by heating a benzene solution of the base with cuprous oxide, or by digesting its warm alcoholic solution with ammoniacal cuprous chloride. The compound is thus obtained in reddish-yellow leaflets decomposing at  $270^{\circ}$ ; when hydrogen sulphide is passed into its benzene solution, cuprous sulphide is precipitated, whilst diazoaminobenzene remains dissolved; it is decomposed explosively by nitric acid at the ordinary temperature. The hydrochloride of the preceding compound,  $(N_2Ph \cdot NCuPh)_2 \cdot 2HCl$ , is obtained by the action of benzyl chloride on a benzene solution of the diazoamino-compound in the presence of copper powder; it consists of light yellow, microscopic needles insoluble in the ordinary solvents and decomposing at  $180^{\circ}$ . The hydrobromide and hydriodide are obtained in a similar manner.

The cupric derivative of diazoaminobenzene, produced by mixing together slightly alkaline alcoholic solutions of the latter and of copper nitrate, forms greenish-black needles, insoluble in alcohol and ether, but soluble in benzene; it melts and decomposes at  $170^{\circ}$ . It is quite possible that the inorganic cuprous and cupric ammonium compounds and the corresponding mercury salts have constitutions analogous to those of the copper derivatives of diazoaminobenzene.

G. T. M.

**Acetophenoneazobilirubin.** By FR. PRÖSCHER (*Zeit. physiol. Chem.*, 1900, 29, 411—415).—In 1883, Ehrlich in his work on the diazo-reaction in urine, showed that bilirubin forms a coloured product with diazobenzenesulphonic chloride. The present communication shows that bilirubin can form monoazo-derivatives also, for example, acetophenoneazobilirubin,  $C_{24}H_{25}O_4N$ , which crystallises in minute needles, black by transmitted, but magenta-coloured by reflected light. It gives characteristic absorption bands which are described fully.

W. D. H.

**Hexon Bases: Lysine.** By YANDELL HENDERSON (*Zeit. physiol. Chem.*, 1900, 29, 320—328).—Eight preparations of lysine from different sources were examined with a view to seeing whether there are several substances included under that name. The result shows that lysine is a single substance. From experiments in which lysine was fused with alkali, the constitution  $NH_2 \cdot [CH_2]_4 \cdot CH(NH_2) \cdot CO_2H$  is assigned to it.

W. D. H.

**Action of Heat, Dilute Acids, and Alcohol on Albuminin.** By ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 249—252. Compare Abstr., 1899, i, 655, and this vol., i, 126, 127).—A compound of albuminin with hydrogen chloride having a constant composition is obtained as follows. A saturated aqueous solution of albuminin is dialysed into water during three days and to the filtered, dialysed solution 4 per cent. hydrochloric acid is added until the liquid is acid to tropeolin OO. The solution is immediately precipitated with a mixture of alcohol and ether and the precipitate washed with alcohol and pressed between filter paper. The substance thus obtained does

not dissolve in water, but only swells up and on heating on the water-bath yields a thick, opalescent solution which will not filter; on adding alcohol and ether, washing the precipitate first with alcohol and then with ether and drying in a current of air, a substance of the composition  $\text{Alb}, 3\text{HCl}$ , where  $\text{Alb} = \text{C}_{144}\text{H}_{225}\text{O}_{50}\text{N}_{37}\text{S}_2$ , is obtained. The action of 0.1 per cent. hydrobromic acid on albumin gives the compound  $2\text{Alb}, 5\text{HBr}$ , whilst dialysis of a solution in 0.2 per cent. phosphoric acid yields the compound  $\text{Alb}, 2\text{H}_3\text{PO}_4$ . Separate portions of a filtered, dialysed, saturated, aqueous solution of albumin were treated as follows: (1) evaporated in a vacuum; (2) precipitated with methyl alcohol and repeatedly washed with the boiling alcohol; (3) precipitated and washed with ethyl alcohol; (4) precipitated by boiling in a sealed tube. All the precipitates on drying at  $100^\circ$  gave on analysis the composition  $\text{C}_{144}\text{H}_{225}\text{O}_{50}\text{N}_{37}\text{S}_2$ , but only that treated as in (1) was soluble in water at the ordinary temperature.

T. H. P.

**Effect of Desiccation of Albumin on its Coagulability.** By J. BRET LAND FARMER (*Proc. Roy. Soc.*, 1900, 66, 329—333).—The temperature at which aqueous solutions of albumin coagulate is not constant even for the same type of albumin. Whilst solutions of albumin from freshly-laid hens' eggs became opalescent at as low as  $60^\circ$  and coagulated at  $64^\circ$ , another sample showed opalescence at  $65.5^\circ$  and coagulated at  $68^\circ$ .

The dried egg albumin employed in the experiments now described dissolved readily in water; the filtered solution became opalescent at  $60^\circ$  and coagulated at  $62$ – $63^\circ$ . When the substance was heated alone for 2–3 hours at  $80^\circ$ , it became insoluble; if, however, it is carefully dried at  $52$ – $55^\circ$ , it may be afterwards kept for many hours at a temperature of  $102$ – $110^\circ$  without undergoing any change, so far as could be observed. When dissolved in water and gradually heated, the solution became opalescent, and coagulated at the same temperatures as before desiccation.

N. H. J. M.

**Invertin.** By MARTIN KÖLLE (*Zeit. physiol. Chem.*, 1900, 29, 429—436).—Osborne showed that his preparation of invertin yielded on decomposition a sugar the nature of which was not determined. It is now shown by the examination of the osazone that the sugar in question is mannose.

W. D. H.

**Preparation of Thymin.** By WALTER JONES (*Zeit. physiol. Chem.*, 1900, 29, 461—466).—The want of knowledge of the constitution of thymin is largely due to the difficulty of obtaining the pure substance from nucleic acid. The method now introduced avoids this by operating directly on herring roe with sulphuric acid; the product is subsequently treated with baryta water, and the thymin ultimately obtained as a silver compound, the solubility of which enables it to be easily separated from other silver salts formed. The method is described in full detail.

W. D. H.

**Preparation of Nucleic Acids.** By P. A. LEVENE (*J. Amer. Chem. Soc.*, 1900, 22, 329—331).—The methods of preparation of nucleic acid which involve heating with alkalis are objectionable,

since they change to some extent the original character of the substance. The following method yields satisfactory results. The nucleoprotein material is digested with solution of sodium hydroxide (5 per cent.) or ammonia (8 per cent.) for 2 hours in a cool place; acetic acid is then gradually added until the solution is only slightly alkaline. The mixture is now neutralised with picric acid in order to remove the proteids, and then rendered strongly acid by the addition of more acetic acid; it is left for some time, filtered, and alcohol added until the whole of the nucleic acid is precipitated. The author has applied this method to the preparation of nucleic acids from ovovitellin, ichthulin of cod-fish eggs, cod-fish sperm, pancreas, and *Bacillus tuberculosis*.  
E. G.

**Nucleic Acid of the Embryo of Wheat and its Protein Compounds.** By THOMAS BURR OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, 22, 379—413).—This paper contains an account in detail of the examination of wheat germs freed from bran and endosperm and ground into meal. This was separated into the following substances (the numbers indicate the percentage of the total nitrogen obtained in the form of each constituent): Insoluble in water and salt solution, 30; globulin (insoluble in water, soluble in salt solution), 19; albumin (soluble in water, coagulable by heat), 30; proteose (soluble in water, not coagulable by heat, precipitated by tannin), 9; (not precipitated by tannin), 11. The globulin and albumin yield a nuclein when digested with pepsin. The nuclein can be precipitated in two parts by dissolving it in dilute alkali and adding, first a slight excess of dilute hydrochloric acid, and then strong hydrochloric acid in considerable quantity to the filtrate from the first precipitate. The first precipitate consists of a protein, the second of a *nucleic acid* with a composition (corrected for ash, as are also the other results quoted) corresponding with that required for the formula  $C_{21}H_{31}O_{15}N_8P_2$ . This acid differs from any nucleic acid hitherto described; when hydrolysed with hot 2 per cent. hydrochloric acid, it yields guanine, adenine, phosphoric acid, and other products, but no sugar.

If it be assumed that the albumin, globulin, and nuclein are compounds of this nucleic acid with substances free from phosphorus, the amount of nucleic acid in each compound can be calculated from the percentage of phosphorus found therein, and by subtracting the amounts of carbon, hydrogen, oxygen, and nitrogen contained in this amount of nucleic acid from the amounts found in the analysis of the globulin, &c., the composition of the other constituent containing no phosphorus can be ascertained. This constituent is to be regarded as the true *protein*, and should alone be designated *albumin*, &c.; it is to be regarded as a poly-acid base (compare Abstr., 1899, i, 836), and the substances of varying composition, actually obtained, as compounds of this base with an acid in varying proportions; the acid being nucleic acid in the present case, the "albumins" in question should be called *nucleoalbumins*. The protein constituents of the nucleins were actually found to have compositions very similar to those of the protein constituents

in the albumin or globulin from which they were derived respectively. Thus, no special distinction can be made between nucleins and nucleoproteids; the former simply contain a relatively greater amount of nucleic acid. The insoluble portion of the wheat germs is probably composed also of a protein and nucleic acid. Probably the substances described do not exist as such in the germs, but are formed, or at least altered in composition, during the manipulation; it seems, generally speaking, that the more insoluble forms contain the larger proportion of nucleic acid. The proteids of the embryo undergo these changes more readily than do those of the dormant endosperm.

The albumin, or better nuclealbumin, was obtained in yield equal to 10 per cent. of the embryo. It coagulates partially at 52—65°; at 100°, about 1/3 more coagulates. It is identical with the leucosin of wheat, rye, barley, and malt (*Abstr.*, 1896, i, 399, 455, 714). The globulin, or better nucleoglobulin, was obtained in 5 per cent. yield; it coagulates at 87—90° when dissolved in 10 per cent. aqueous sodium chloride. The proteose was separated by salting-out into two parts, one insoluble, the other soluble, in saturated salt solution.

The composition of the substances obtained is given below; in most cases, the number quoted is the mean of several results.

	C.	H.	O (diff.).	N.	S.	P.	
Nucleic acid.....	36.48	4.48	33.91	16.17	—	8.96	
Leucosin*.....	52.65	7.04	22.56	16.43	1.32	—	
Globulin* .....	51.57	7.07	22.11	18.60	0.65	—	
Proteose..... {	insol.	49.94	6.80	24.94	17.08	1.24	—
	sol....	48.65	6.75	26.82	16.68	1.10	—

\* After subtracting the nucleic acid.

C. F. B.

**Protein Constituents of Egg White.** By THOMAS BURR OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, 22, 422—450. Compare *Abstr.*, 1899, i, 836).—A large quantity of white of egg was subjected to fractional precipitation with ammonium sulphate; 6 litres from 240 eggs yielded 500 grams of protein substances, and of these 280 grams were separated in crystalline form. The substance, hitherto regarded as globulin, which is precipitated by diluting white of egg, is nearly all ovomucin (*Eichholz*, *Abstr.*, 1898, ii, 541), and forms about 7 per cent. of the proteid matter. It coagulates in aqueous sodium chloride solution at 75—78°, and does not dissolve in 1 per cent. sodium carbonate solution.

The substance precipitated in the crystalline form by ammonium sulphate is ovalbumin; this portion forms 50 per cent. of the proteid matter, and more ovalbumin is contained in the other fractions, so that it is the chief constituent of white of egg. The influence of concentration on the coagulation was studied, and also that of sodium chloride and of hydrochloric and acetic acids; the point of coagulation falls slightly with increasing concentration of the ovalbumin, but rises with increasing percentage of sodium chloride. The specific rotation,  $[\alpha]_D$ , was -28.60° to -30.80° in different fractions. The carbo-

hydrate, which was eliminated from ovalbumin by boiling the latter with 3 per cent. hydrochloric acid for  $\frac{1}{2}$  hour, yielded a phenylosazone which melted at  $187-189^{\circ}$ , and had not quite the same appearance as phenylglucosazone. It is thought to be derived undoubtedly from the ovalbumin, and not from any ovomucoid present as an impurity. Its amount is probably 3—5 per cent. of the ovalbumin.

The fractions remaining after separation of the ovalbumin in the crystalline form yield, at  $65^{\circ}$ , a coagulum of *conalbumin*; at  $90^{\circ}$ , another coagulum containing ovalbumin, conalbumin, and ovomucoid, whilst ovomucoid remains in solution. Conalbumin resembles ovalbumin in properties and composition; hence its name. From solutions in 10 per cent. aqueous sodium chloride it coagulates at  $55-60^{\circ}$ ; in aqueous solution only, it is not completely coagulated before the ovalbumin begins to separate. The specific rotation was determined in 10 per cent. aqueous sodium chloride solution containing also ovalbumin and ovomucoid; allowing for the rotation due to these, it was found to be  $[\alpha]_D - 36^{\circ}$  to  $-39^{\circ}$ .

Ovomucoid was found to have the specific rotation  $-61^{\circ}10'$  to  $-61^{\circ}38'$ .

The composition of the four substances was:

	C.	H.	O (diff.).	N.	S.	P.
Ovomucin .....	50.82	6.88	25.64	14.66	1.94—2.28	—
Ovalbumin....	52.75	7.10	22.90	15.51	1.62	0.12
Conalbumin...	52.25	6.99	22.95	16.11	1.70	—
Ovomucoid ...	48.96	6.53	29.71	12.44	2.36	—

C. F. B.

**Schinoxydase, an Oxydase present in Schinus Molle.** By J. SARTHOU (*J. Pharm.*, 1900, [vi], 11, 482—488).—The latex of *Schinus molle* is a milky fluid which on exposure to the air becomes bluish in colour, and finally brown. This colour change is effected by an enzyme, *schinoxydase*, which is capable of rapidly bringing about the oxidation of quinol, resorcinol, pyrogallol, and potassium ferrocyanide, by means of atmospheric oxygen, and is hence an aeroxidase. The enzyme can be isolated by precipitating an emulsion of the latex formed with water by means of alcohol of  $95^{\circ}$  sufficiently large in amount to dissolve the resin present; it is obtained as a white, flocculent precipitate, which is easily soluble in water; the aqueous solution acts as an oxidising agent with the substances named. When the oxydase is dehydrated, either by leaving it in contact for several minutes with alcohol of  $95^{\circ}$ , or in a vacuum, it temporarily loses its oxidising power, although this is immediately restored on rehydration; on the other hand, the enzyme, when left for 24 hours in contact with alcohol, loses its flocculent appearance and becomes coagulated, whilst its properties as an oxydase are permanently destroyed.

W. A. D.

**Function of Iron in Schinoxydase.** By J. SARTHOU (*J. Pharm.*, 1900, [vi], 11, 583—589. Compare preceding abstract).—The ash of schinoxydase contains a considerable quantity of iron, calcium, and

sodium, but no manganese; since the oxidising power of the latex of *Schinus molle* is nearly proportional to the amount of iron it contains, the author considers that iron plays the same part in schinoxydase in promoting oxidation as manganese in Bertrand's laccase.

The action of a number of ferrous salts in promoting the oxidation of easily oxidisable substances by atmospheric oxygen is dealt with, and the following conclusions may be drawn. (1) That iron, in the form of salts of carboxylic acids, is only slightly capable of promoting oxidation, but is very active in the form of ferrous cyanide and ferrous ammonium sulphate, although slightly less rapid with the latter than with the former. (2) Ferrous hydroxide, washed free from alkali, is also very active; it is noteworthy that the amount of oxygen absorbed by the hydroxide in presence of quinol is much greater than that which is absorbed, under similar conditions, by the ferrous hydroxide alone, although the quinol alone is non-absorbent. (3) Finally, for the same quantity of iron, the amount of oxygen rendered active depends on the state of combination of the iron. W. A. D.

**Proteolytic Diastase of Malt.** By AUG. FERNBACH and L. HUBERT (*Compt. rend.*, 1900, 130, 1783—1785).—The coagulable albumin of filtered malt extract, prepared at the ordinary temperature, becomes non-coagulable when the solution is digested at temperatures below 70°. This change is not due to microbes, for a similar result is obtained in media sterilised by means of a Chamberland filter, neither is it brought about by the dissolved salts, for the action is prevented by warming the solution. The cold sterilised extract renders gelatin soluble, whereas the heated solution has no effect on this substance. These results point to the presence of a proteolytic diastase in the malt extract. By treating the solution with alcohol, a precipitate is obtained which has a solvent action on the coagulable albumin of malt extract, and also on the insoluble nitrogenous compounds of the barley grain. This action commences at 40°, reaches its maximum at 60°, and is still very marked at 70°.

The nature of the soluble products formed from the malt proteids during brewing by the proteolytic diastase, varies with the temperature of digestion. On applying the phosphotungstic acid test, it is found that at 40° the soluble nitrogen is wholly present in amino-compounds, whilst at 60° and 70° the aminic nitrogen forms only 50—60 and 40 per cent. respectively of the total quantity of this element present in solution. G. T. M.

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## Organic Chemistry.

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**Configuration and Classification of Aliphatic Compounds.** By FRIEDRICH KRAFFT (*J. pr. Chem.*, 1900, [ii], 62, 75—82. Compare Petrenko-Kritschenko, this vol., i, 421).—An account is given of the gradual disappearance of the line of separation between the fatty and aromatic compounds. The special properties of the carbon atom in both series of compounds is regarded as depending, not only on its quadrivalency, but also on the fact that it has the smallest atomic volume of all the elements. T. M. L.

**Hydrocarbons in Heavy Texas Petroleum.** By CHARLES F. MABERY and D. M. BUCK (*J. Amer. Chem. Soc.*, 1900, 22, 553—556).—The crude oil examined was thick and of a dark colour; it contained 0.94 per cent. of sulphur and appreciable quantities of water, and had a sp. gr. 0.950 at 20°. By the aid of fractional distillation under diminished pressure, and removal of benzene hydrocarbons by fuming sulphuric acid, the following compounds have been isolated:  $C_{14}H_{26}$ , 125—130°, sp. gr. 0.8711;  $C_{15}H_{28}$ , 140—145°, sp. gr. 0.8788;  $C_{16}H_{30}$ , 160—165°, sp. gr. 0.8894;  $C_{17}H_{34}$ , 175—180°, sp. gr. 0.8966;  $C_{19}H_{36}$ , 195—200°, sp. gr. 0.902;  $C_{21}H_{38}$ , 215—220°, sp. gr. 0.9163;  $C_{25}H_{46}$ , 270—275°, sp. gr. 0.941. The boiling points given are all under a pressure of 25 mm.

In order to avoid decomposition of the higher fractions, they were first mixed with light petroleum before treatment with fuming sulphuric acid. J. J. S.

**Norwegian Tar.** By KNUT T. STROM (*Bied. Centr.*, 1900, 29, 574—575; from *Kristiania Videnskabs-Selskabs Verhand.*, 1899).—The tar was obtained by burning pine-wood in holes in the ground. It contained 4.75 per cent. of acids (as acetic acid), 10.94 per cent. of phenols, and 60.80 per cent. of hydrocarbons and other indifferent substances. Sp. gr. 1.068 at 15°. Formic, acetic, propionic, *n*-butyric, valeric, methylpropylacetic, *n* caproic, cenanthoic, *n*-caprylic, and possibly pelargonic, capric, and (inactive) pimic acids, cresol guaiacol, ethyl- and propyl-guaiacol, a compound,  $C_{11}H_{16}O_2$  (perhaps methylpropyl-guaiacol), in the fraction boiling at 250—255°, and a compound,  $C_{12}H_{14}O_2$ , in the distillate which boiled at over 300° were found.

The hydrocarbons and other indifferent substances (14 per cent. solid and 86 per cent. liquid) included retene and terpenes.

N. H. J. M.

**General Method for the Preparation of Halogen Derivatives of Aliphatic Hydrocarbons.** By ANTOINE MOUNEYRAT (*Ann. Chim. Phys.*, 1900, [vii], 20, 485—574).—A detailed account of work already published (*Abstr.*, 1898, i, 613, 625; 1899, i, 1, 97, 241, 247, 311, 397, 470, 555, 556, 725, 786). W. A. D.

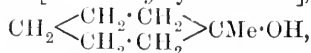
**Electrolytic Syntheses of Organic Substances. II. (Iodoform.)** By OCTAVE DONY-HÉNIAULT (*Zeit. Elektrochem.*, 1900, 7, 57).—The discharge potential of iodine ions in a solution containing sodium

carbonate is not diminished by the presence of alcohol. The author concludes, therefore, that the formation of iodoform is not to be attributed to the direct action of iodine on alcohol. It is probably due to the action of hypoiodite,  $\text{EtOH} + 5\text{HIO} = \text{CHI}_3 + \text{CO}_2 + 2\text{HI} + 4\text{H}_2\text{O}$ , the small (and variable) quantity of iodate formed being due to the change  $3\text{HIO} = \text{HIO}_3 + 2\text{HI}$ . The author shows that the second change is retarded by the presence of either iodide or iodate, and that the yield of iodoform, from a given quantity of iodine, is therefore greater in presence of excess of these substances. He also shows that iodoform is produced by the action of a solution of hypoiodous acid (made by shaking together iodine, mercuric oxide, and water) on a solution of alcohol, potassium iodide, and sodium carbonate at  $60^\circ$ . That chloroform and bromoform cannot be made by the electrolytic method is due to the fact that the discharge potentials of chlorine and bromine are higher than that of hydroxyl. Oxidation products of alcohol are therefore produced instead of chloroform or bromoform. T. E.

**New Method for the Preparation of Nitromethanes.** By VICTOR AUGER (*Bull. Soc. Chim.*, 1900, [iii], 23, 333—336).—When potassium chloroacetate is heated with sodium nitrite in concentrated aqueous solution, carbon dioxide is evolved and nitromethane is formed. The author finds that many of the nitroparaffins may be obtained by means of this reaction, and details are given in the paper of the preparation of nitroethane from  $\alpha$ -bromopropionic acid, nitropropane from  $\alpha$ -bromobutyric acid, nitroisobutane from  $\alpha$ -bromoisovaleric acid, and nitrohexane from  $\alpha$ -bromoheptonic acid.  $\alpha$ -Bromoisobutyric acid and active valeric acid (methylethylacetic acid), when treated with sodium nitrite, yield isopropylpseudonitrole and  $\beta$ -butylpseudonitrole respectively. No definite products could be obtained from  $\alpha$ -bromopalmitic acid. N. L.

**Tertiary Derivatives of Heptanaphthene [Methylcyclohexane].** By WLADIMIR B. MARKOWNIKOFF and WLADIMIR TCHERDINTZEFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 302—303).—[With EFIMOFF.] — *tert.-Nitroheptanaphthene* [1-nitro-1-methylcyclohexane],  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CMe} \cdot \text{NO}_2$ , is a liquid with an odour resembling that of turpentine; it boils at  $109\text{--}110^\circ$  under 40 mm. pressure, has the sp. gr. 1.0367 at  $0^\circ/0^\circ$  and 1.025 at  $20^\circ/0^\circ$ , and on cooling solidifies to a glassy mass melting at  $-71^\circ$ . The corresponding *amine*,  $\text{C}_7\text{H}_{15}\text{N}$ , boils at  $141^\circ$  and solidifies to a vitreous mass melting at  $-96^\circ$ ; the *hydrochloride* melts at  $256\text{--}257^\circ$ ; the salts are in general readily soluble, but the *sulphate*, crystallising in plates, and the *oxalate*, in leaflets, are only slightly soluble; the *platinichloride* (with  $\text{H}_2\text{O}$ ) forms beautiful, brick-red octahedra and tetrahedra; the slightly soluble *aurichloride* separates in golden-yellow needles, and the *auribromide* in flat, dark brown needles.

*tert.-Heptanaphthenol* [1:1-methylcyclohexanol],

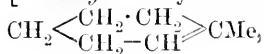


obtained by diazotising the salts of the amine, boils with partial decomposition at  $155^\circ$  under 742 mm. pressure. It solidifies on cooling,



and melts at  $12^{\circ}$ . The corresponding *chloride*,  $C_6H_{10}MeCl$ , boils at  $53-55^{\circ}$  under 40 mm. and, under ordinary pressure, at  $148-151^{\circ}$  with decomposition.

$\alpha$ -(or 1:2)-*Naphthylene* [1-methyl- $\Delta^{1,2}$ cyclohexene],



boils at  $108^{\circ}$  under 747 mm. pressure.

T. H. P.

**Secondary Derivatives of Heptanaphthene** [Methylcyclohexane. By WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 303-305).—The physical constants of several secondary heptanaphthene derivatives, previously obtained by Wallach (*Abstr.*, 1896, i, 309) and Zelinsky (*Abstr.*, 1897, i, 462), have been revised.

$\beta$ -Methylnaphthanol [1:3-Methylcyclohexanol] is a viscous liquid which boils undecomposed at  $173.7-174^{\circ}$  under 769 mm. pressure, and solidifies to a glassy mass melting at  $-47^{\circ}$ ; it has the sp. gr. 0.9286 at  $0^{\circ}/0^{\circ}$ , and 0.9158 at  $20^{\circ}/0^{\circ}$ , and the specific rotation  $[\alpha]_D 3^{\circ}44.1'$ ; it dissolves in 97 volumes of water. The halogen derivatives of this naphthanol consist of mixtures of two isomerides. Thus the chloride under ordinary pressure decomposes into hydrogen chloride and the hydrocarbon  $C_7H_{12}$ , which boils at  $156-159^{\circ}$ ; but on treating the chloride with alcoholic potash, the greater part is decomposed into the naphthylene boiling at  $103^{\circ}$ , whilst the remaining chloride boils undecomposed at  $160-161^{\circ}$ . The iodide, after the same treatment, boils at  $200-205^{\circ}$  without decomposition. The  $\beta$ -naphthylene (2:3) boils at  $103^{\circ}$  under 768 mm. pressure.

T. H. P.

**Erythritol in Trentepohlia Jolithus.** By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1900, 21, 571-573).—The alga *Trentepohlia Jolithus* (*Chroolepus Jolithus*), when extracted with ether, yields erythritol and a ruby-red, sticky mass, which is coloured an intense blue with concentrated sulphuric acid.

R. H. P

**Some Phosphoric Esters.** By JACQUES CAVALIER and EUGÈNE PROST (*Bull. Soc. Chim.*, 1900, [iii], 23, 678-681. Compare this vol., i, 75).—*n*-Propyl, isopropyl, and isobutyl phosphates are analogous to the methyl and ethyl esters, and are obtained in a similar manner, the trialkyl phosphates by heating together mol. proportions of silver phosphate and alkyl iodide, and the mono- and di-alkyl phosphates by the action of phosphoric oxide on the alcohols, the separation of the latter esters being effected by means of their barium salts.

*Tripropyl phosphate*,  $PO_4Pr^{\alpha}_3$ , is a colourless liquid which is slightly soluble in water, and boils without decomposition at  $138^{\circ}$  under 47 mm. pressure, and at  $133.5^{\circ}$  under 22 mm. pressure. *Lead dipropyl phosphate*,  $(PO_4Pr^{\alpha}_2)_2Pb$ , crystallises in small, anhydrous needles melting at  $145-147^{\circ}$ ; it decomposes at about  $210^{\circ}$  with the formation of tripropyl phosphate and the salt  $PO_4Pr^{\alpha}Pb$ . *Barium monopropyl phosphate*,  $PO_4Pr^{\alpha}Ba + 2H_2O$ , is efflorescent; 100 parts of the aqueous solution contain 8.08 of the anhydrous salt at  $20.5^{\circ}$ , 6.98 at  $60^{\circ}$ , and 3.87 at  $85^{\circ}$ .

*Triisopropyl phosphate*,  $PO_4Pr^{\beta}_3$ , is a colourless liquid of agreeable odour, which boils at  $136^{\circ}$  under 68 mm. pressure, and is insoluble in water. *Barium monoisopropyl phosphate*,  $PO_4Pr^{\beta}Ba + 2H_2O$ , crystallises

in nacreous scales; the weight of the anhydrous salt contained in 100 parts of the aqueous solution is 3.52 at 16°, 3.16 at 50°, and 1.7 at 85°.

*Triisobutyl phosphate* could only be obtained in an impure state, since it decomposes on distillation, even under diminished pressure. *Lead diisobutyl phosphate* forms small crystals melting at 169–170°, and is very soluble in water. *Barium monoisobutyl phosphate* crystallises with 2H<sub>2</sub>O and is efflorescent; 100 parts of the aqueous solution contain 5.65 of the anhydrous salt at 24°, 3.30 at 52°, and 2.57 at 85°.

The solubility in water of the trialkyl phosphates decreases with increasing molecular weight, the methyl and ethyl esters being miscible with water in all proportions, whilst the butyl salt is insoluble. The lead salts, (PO<sub>4</sub>R<sub>2</sub>)<sub>2</sub>Pb, where R is methyl, ethyl, propyl, *isopropyl*, or *isobutyl*, are more soluble in hot than in cold water, but the solubility of the barium salts of the composition PO<sub>4</sub>RBa decreases as the temperature rises, except in the case of the ethyl compound, which possesses a maximum solubility at 40°. The amyl derivatives are different in character, the lead and barium salts being almost insoluble in water.

N. L.

**Mixed Anhydrides of Formic Acid.** By AUGUSTE BÉHAL (*Ann. Chim. Phys.*, 1900, [vii], 20, 411–432).—Most of the facts dealt with in this paper have already appeared (*Abstr.*, 1899, i, 734), but the following are new.

*sec-Octyl formate*, obtained by the interaction of *sec*-octyl alcohol and formic acetic anhydride, boils at 186–187° under the ordinary pressure, and has a sp. gr. 0.8852 at 0°; its odour resembles that of cucumber.

Allyl formate boils at 87°, not at 82–83° as stated by Tollens (*Zeit. Chem.*, 1866, 2, 18; 1868, 4, 41).

The product obtained by acting on linalool with formic acetic anhydride boils at 125–127° under 30 mm. pressure, and has a sp. gr. 0.9672 at 0°; it consists probably of a mixture of *linalyl* and *gerunyl* formates, since on hydrolysis it yields linalool and geraniol.

*Benzyl formate* boils at 202–203° under 747 mm. pressure, and has a sp. gr. 1.081 at 23°.

*d*-Bornyl formate (Bertram and Walbaum, *Abstr.*, 1893, i, 659, and 1894, i, 204) boils at 106–108° under 21 mm. pressure, and has a sp. gr. 1.027 at 0°, and 1.009 at 22°;  $[\alpha]_D + 48^\circ 45'$ . *l*-Bornyl formate boils at 106–108° under 21 mm. pressure, has a sp. gr. 1.026 at 0°, and 1.009 at 22°, and  $[\alpha]_D - 48^\circ 56'$  (compare Tschugaeff, *Abstr.*, 1898, ii, 495).

Terpinyl formate, obtained from terpinol melting at 35°, boils at 127–128° under 30 mm., and has a sp. gr. 0.9945 at 0° (compare Lafont, *Abstr.*, 1888, 495).

*Menthyl formate* boils at 219° under the ordinary pressure, and has a sp. gr. 0.9499 at 0°, and 0.9396 at 15°;  $[\alpha]_D - 80.17$ .

*Cinnamyl formate* boils at 138–139° under 23 mm. pressure, and has a sp. gr. 1.086 at 0°.

*Caryophyllenyl formate* boils at 165–167° under 20 mm. pressure, and has a sp. gr. 1.0266 at 0°.

*Santalyl formate* boils at 175—178° under 27 mm. pressure, and has a sp. gr. 1·0180 at 0°.

The monoformic and diformic esters of glycols can usually be purified only with difficulty. *Glycol diformate*,  $C_4H_6O_4$ , boils at 88—89° under 25 mm. pressure, and has a sp. gr. 1·193 at 0°. *Pinacone monoformate*,  $C_7H_{14}O_3$ , boils at 90° under 20 mm. pressure. *Styrolene diformate*,  $C_{10}H_{10}O_4$ , boils at 164—165° under 25 mm. pressure, and has a sp. gr. 1·2091 at 0°. *Terpin diformate*,  $C_{12}H_{20}O_4$ , is a viscous liquid with an orange-like odour; it boils at 176—177° under 40 mm. pressure, and has a sp. gr. 1·067 at 27°.

Monoformin, diformin, or triformin could not be obtained by combining glycerol with formic acetic anhydride, owing to the acetyl radicle of the mixed anhydride entering into action to yield *glyceryl acetodiformate*,  $C_7H_{10}O_6$ ; this boils at 157° under 27 mm. pressure, and has a sp. gr. 1·249 at 0°.

Formic acetic anhydride does not act on phenols in the cold, but on warming, acetates, and not formates, are obtained. With ammonia or primary or secondary amines, the corresponding formamides are produced. Methylformanilide,  $NMePh \cdot CHO$ , melts at 8°, boils at 142° under 20 mm. pressure, and has a sp. gr. 1·107 at 0°. *o*-Formaminophenol,  $CHO \cdot NH \cdot C_6H_4 \cdot OH$ , crystallises from water or from a mixture of benzene and alcohol, and melts at 125°. *p*-Ethoxyformanilide,  $OEt \cdot C_6H_4 \cdot NH \cdot CHO$ , crystallises from water and melts at 68·5°. *o*-Phenylenediamine does not give rise to a formamide, but yields phenylmethenylamidine,  $C_6H_4 \langle \begin{smallmatrix} N \\ NH \end{smallmatrix} \rangle CH$  (Wundt, Abstr., 1878, 667).

Formic acid interacts with propionic, butyric, and isovaleric anhydrides, apparently yielding mixed anhydrides analogous to formic acetic anhydride; like the latter, they are decomposed by tertiary bases, yielding carbon monoxide; *sec*-octyl alcohol in all cases gives rise to *sec*-octyl formate.

Incidentally, a method of estimating formic acid by means of iodic acid is described, based on the reaction  $2HI O_3 + 5HCO_2H = 5CO_2 + 6H_2O + I_2$ ; a weighed quantity of the substance containing formic acid is boiled for 1 hour in a reflux apparatus with 20 c.c. of a 50 per cent. solution of iodic acid, the iodine thus liberated distilled into aqueous potassium iodide, and titrated against sodium thiosulphate.

W. A. D.

**Reduction of Oleic to Stearic Acid by the Aid of Nascent Hydrogen.** By J. FREUNDLICH and OTTO ROSAUER (*Chem. Zeit.*, 1900, 24, 566).—The authors have tried Tissier's method for the reduction of oleic acid by the aid of water and granulated zinc under pressure; they find that the amount of stearic acid formed is small (1·7—3·79 per cent.), but that considerable quantities of zinc soaps are produced.

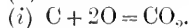
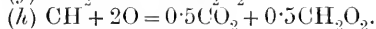
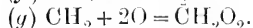
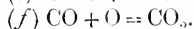
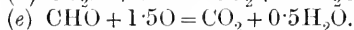
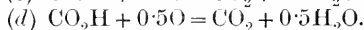
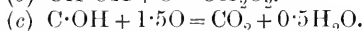
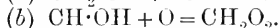
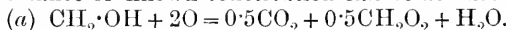
J. J. S.

**Campholytic and isoLauronolic Acids.** By G. BLANC (*Bull. Soc. Chim.*, 1900, [iii], 23, 695—701).—When the nitrile,  $C_{15}H_{21}CN$ , which Forster (*Trans.*, 1899, 75, 1141) obtained from camphoroxime, is reduced with sodium and boiling alcohol, it is converted into

$\alpha$ -aminocampholene, which was identified by means of its ureide and oxamide. The greater part of the paper is devoted to a discussion of the bearing of this result and of the researches of Forster (*loc. cit.*) and Walker (Trans., 1893, 63, 495; 1895, 67, 347; 1900, 77, 374) on the constitution of campholytic and isolauronic acids. N. L.

**Glycollic and Glyoxylic Acids.** By CARL BOETTINGER (*Chem. Zeit.*, 1900, 24, 619—620).—Glycolloglycollic acid, together with a small amount of glycollide, is formed when glycollic acid is boiled for 2 hours with acetic anhydride or when the acid is treated with boric and acetic anhydrides; when rapidly distilled, it passes over unaltered, otherwise it rapidly chars. The acid is readily hydrolysed to glycollic acid, and its calcium salt has the composition  $(C_4H_5O_5)_2Ca, 2H_2O$ . No well-defined products have been obtained by the action of acetic anhydride on glyoxylic acid. The following salts of glyoxylic acid have been prepared,  $C_2HO_3K, H_2O$  and  $(C_2HO_3)_2Ba, 4H_2O$ . J. J. S.

**Oxidation of Dibasic Acids of the Aliphatic Series by Acid Potassium Permanganate.** By LÉON PERDRIX (*Bull. Soc. Chim.*, 1900, [iii], 23, 645—660).—It has been previously shown (Abstr., 1897, i, 177) that the majority of polyhydric alcohols and their derivatives are oxidised by acidified potassium permanganate solution at the boiling temperature to carbon dioxide, formic acid, and water, the relative proportion of these products depending on the constitution of the substance oxidised. In the present paper, the behaviour of a number of acids is studied, and the following extended table representing the modes of oxidation of the different atomic groups is given. From these data, the equation representing the oxidation of a substance of known constitution can be at once deduced.



These results are shown to hold for mesoxalic, acetonedicarboxylic, itaconic, citric, fumaric, and maleic acids. Adipic, pimelic, and suberic acids resemble succinic acid in being scarcely, if at all, attacked by acidified potassium permanganate. Alkyl groups in side chains are not destroyed on oxidation, and when connected with a CH group the equation  $R \cdot CH + 2O = R \cdot CO_2H$  is found to hold. Thus, isosuccinic acid yields acetic acid, and ethylmalonic acid yields propionic acid. Lactide and pyrotartaric, citraconic, and mesaconic acids are other examples of this class. N. L.

**Substitution Products of Tetroneic Acid.** By LUDWIG WOLFF (*Annalen*, 1900, 312, 119—132. Compare Abstr., 1896, i, 522).—An introduction to the following papers. M. O. F.

**Nitrotetronic Acid, Aminotetronic Acid, and their Derivatives.** By LUDWIG WOLFF and A. LÜTTINGHAUS (*Annalen*, 1900,

312, 133—155).—*Nitrotetronic acid*,  $\text{OH}\cdot\text{NO}\cdot\overset{\text{CO}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}>\text{O}$ , prepared

by the action of fuming nitric acid on tetronic acid, and also by oxidising oximinotetronic acid (Abstr., 1896, i, 524) with nitric or chromic acid, crystallises from hot water in lustrous prisms containing  $2\text{H}_2\text{O}$ , and melts, evolving gas, at  $184^\circ$ ; the *barium* salt separates from hot water in triclinic crystals containing  $4\text{H}_2\text{O}$ , and the *silver* salt contains  $1\text{H}_2\text{O}$ . The *hydroxylamine* salt forms nacreous leaflets and melts at  $194$ — $195^\circ$ , evolving gas; the *methyl* ether crystallises from alcohol or water in small, yellowish, six-sided plates, and melts at

$143$ — $144^\circ$ , evolving gas. The *phenylhydrazone*,  $\text{NHPh}\cdot\text{N}\cdot\overset{\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}>\text{O}$ , is sparingly soluble in common media, crystallises from glacial acetic acid in small, yellowish-brown prisms, and melts at  $184$ — $186^\circ$ , when

it decomposes. The *oxime*,  $\text{NOH}\cdot\overset{\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}>\text{O}$ , crystallising from hot water in white, lustrous plates or prisms containing  $1\text{H}_2\text{O}$ , becomes yellow at  $140^\circ$ , and melts, evolving gas, at  $147^\circ$ ; the *silver* salt is crystalline, and the *barium* salt forms aggregates of pale yellow needles, whilst the *methyl* ether separates from methyl alcohol in pale yellow, six-sided plates melting and decomposing at  $154$ — $155^\circ$ .

*Aminotetronic acid*,  $\text{OH}\cdot\overset{\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}>\text{O}$ , prepared by reducing nitrotetronic acid with sodium amalgam, or, in acid solution, with zinc or tin, crystallises from dilute alcohol in colourless needles, which become yellow at  $150^\circ$  and char above  $250^\circ$ ; it is very readily soluble in water, the solution, which is acid, decomposing carbonates, and developing a pale red coloration with ferric chloride. The *dibenzoyl* derivative crystallises from alcohol or benzene in slender needles melting at  $164^\circ$ , and is readily hydrolysed to the *benzoyl* derivative,

$\text{OH}\cdot\overset{\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}>\text{O}$ , which crystallises in long needles or four-sided prisms, and melts at  $178^\circ$ ; boiling aniline converts the latter substance into the *anilide* of benzoylamino-tetronic acid, which crystallises from alcohol in colourless prisms and melts at  $191$ — $192^\circ$ .

The *anhydride* of diazotetronic acid,  $\text{N}\leq\overset{\text{O}\cdot\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{N}\cdot\text{C}}}>\text{O}$ , produced when aminotetronic acid is treated with nitrous acid, crystallises from a mixture of chloroform and petroleum in lustrous, four-sided plates, and melts at  $93^\circ$ ; aqueous or acid solutions are stable towards iodine, hydroxylamine hydrochloride, sulphurous acid, or oxidising agents, but alkalis, and solutions of alkali salts such as sodium acetate, nitrite, or cyanide, decompose it rapidly. The aqueous solution develops a colouring matter with the sodium derivative of  $\alpha$ -naphthol. *Glycolloglycollic acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , results from hydrolysing diazotetronic anhydride with barium hydroxide, and crystallises from ether in colourless prisms or six-sided plates melting at  $99$ — $100^\circ$ ; the *calcium* salt contains  $4\frac{1}{2}\text{H}_2\text{O}$ .

*Sodium diazotetrono-sulphonate*,  $\text{ONa} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{SO}_2 \cdot \text{Na} \cdot \text{N} : \text{N} \cdot \text{C} \cdot \text{CO} > \text{O}$ , prepared by treating diazotetronic anhydride with sodium sulphite, crystallises from water in small, pale yellow needles containing  $3\text{H}_2\text{O}$ ; the aqueous solution is neutral, and reduces ammoniacal silver nitrate, mercuric chloride, and Fehling's solution. The *hydrogen potassium salt*,  $\text{C}_4\text{H}_3\text{O}_3\text{N}_2 \cdot \text{SO}_3\text{K}$ , is much less readily soluble than the sodium salt, and crystallises from water in aggregates of lustrous yellow needles or leaflets.

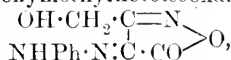
The *anhydride* of dihydrodiazotetronic acid,  $\text{NH} < \text{O} - \text{C} \cdot \text{CH}_2 \cdot \text{NH} - \text{C} \cdot \text{CO} > \text{O}$ , formed on adding the finely powdered sodium salt of diazotetrono-sulphonic acid to concentrated hydrochloric acid, crystallises from water or alcohol in yellowish leaflets melting and decomposing at  $190^\circ$ ; it is readily oxidised to the anhydride of diazotetronic acid, merely boiling an alcoholic solution sufficing to effect this change. Aqueous hydroxylamine hydrochloride converts the anhydride into the compound  $\text{C}_4\text{H}_5\text{O}_3\text{N}_3$ , which may be represented by one of the formulæ,  $\text{NH} < \text{C} < \text{C}(\text{N} \cdot \text{OH}) > \text{CH}_2$  and  $\text{NH} < \text{N}(\text{OH}) \cdot \text{C} \cdot \text{CH}_2 \cdot \text{NH} - \text{C} \cdot \text{CO} > \text{O}$ ; it crystallises from much boiling water in small, yellowish needles, which become brown about  $220^\circ$ , and undergo profound decomposition at about  $250^\circ$ . When suspended in water, the oxime quickly reduces mercuric chloride, losing nitrogen and becoming converted into  *$\beta$ -oximinobutyrolactone*,  $\text{NOH} \cdot \text{C} - \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} > \text{O}$ , which crystallises from hot water in colourless, four-sided plates, and decomposes at  $146^\circ$ ; nitrous acid converts it into dioximinobutyrolactone (compare *loc. cit.*).

M. O. F.

**Phenylhydrazone of Diketobutyrolactone.** By LUDWIG WOLFF and A. LÜTTRINGHAUS (*Annalen*, 1900, 312, 155—162).—The *phenylhydrazone* of diketobutyrolactone,  $\text{NHPh} \cdot \text{N} : \text{C} \cdot \text{CH}_2 \cdot \text{CO} > \text{O}$ , prepared by adding freshly diazotised aniline to an aqueous solution of potassium tetronate, crystallises from glacial acetic acid in small, golden yellow needles, and melts, evolving gas, at  $210^\circ$ ; it reduces Fehling's solution, and develops a deep blue coloration with concentrated sulphuric acid and potassium dichromate. The phenylhydrazone dissolves in ammonia, or sodium hydroxide or carbonate, forming yellow salts of an unstable, monobasic, benzeneazotetronic acid; the *calcium salt* forms yellow needles, and the *silver salt* is also crystalline. The *benzoyl derivative* crystallises from a mixture of chloroform and petroleum in brick-red prisms, and melts at  $142^\circ$ .

The *osazone* of diketobutyrolactone,  $\text{NHPh} \cdot \text{N} : \text{C} \cdot \text{CH}_2 \cdot \text{NHPh} \cdot \text{N} : \text{C} \cdot \text{CO} > \text{O}$ , produced by the action of phenylhydrazine on the phenylhydrazone, crystallises from boiling acetic acid in red plates which decompose at  $242^\circ$ , and in orange-yellow needles which become red at  $180^\circ$ , and melt also at  $242^\circ$ , when they decompose; it is insoluble in sodium carbonate, but yields a yellowish-red solution in hot sodium hydroxide.

The *phenylhydrazoxime* of diketobutyrolactone,  $\text{NOH}\cdot\text{C}(\text{CH}_2)_2\text{CO}>\text{O}$ ,  
 $\text{NHPh}\cdot\text{N}:\text{C}-\text{CO}>\text{O}$ ,  
 obtained by the action of hydroxylamine hydrochloride on the phenylhydrazone, crystallises from boiling alcohol in yellowish-green needles, melting and decomposing at  $236^\circ$ . Hydrolysis resolves this compound into the acid,  $\text{NOH}\cdot\text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{N}\cdot\text{NHPh}$ , which crystallises from dilute alcohol in lustrous yellow needles decomposing at  $147-148^\circ$ . When the alcoholic solution of the acid is boiled with dilute hydrochloric acid, the phenylhydrazoxime is regenerated, but the action of boiling 30 per cent. acetic acid converts it into the *phenylhydrazone* of hydroxymethylketoisooxazolone,



which crystallises from boiling alcohol in lustrous, golden-yellow needles melting and decomposing at  $165^\circ$ ; the *silver* salt is very sparingly soluble in water. M. O. F.

**Behaviour of  $\alpha$ -Methyltetronic Acid towards Diazobenzene Chloride.** By LUDWIG WOLFF and WILLY HEROLD (*Annalen*, 1900, 312, 163—164).—The *phenylhydrazone* of pyruvoglycollic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CMe}\cdot\text{N}\cdot\text{NHPh}$ , prepared by adding diazobenzene chloride to  $\alpha$ -methyltetronic acid, crystallises from hot water in pale yellow needles containing  $2\text{H}_2\text{O}$ ; the anhydrous acid melts at  $163-164^\circ$ , and the solution in concentrated sulphuric acid develops a deep red coloration with potassium dichromate.

Boiling water resolves the substance into glycollic acid and the phenylhydrazone of pyruvic acid. M. O. F.

**Iodotetronic Acid and Sulphotetronic Acid.** By LUDWIG WOLFF and EDUARD FERTIG (*Annalen*, 1900, 312, 164—170).—*Iodo-*

*tetronic acid*,  $\text{OH}\cdot\text{C}(\text{CH}_2)_2\text{CO}>\text{O}$ ,  
 $\text{Cl}\cdot\text{CO}>\text{O}$ , prepared by the action of iodine on tetronic acid in presence of iodic acid, crystallises from hot water in small, white needles, which become coloured on exposure to light, and melts and decomposes at  $178-180^\circ$ ; it is strongly acidic, and develops a violet-red coloration with ferric chloride. Sodium nitrite solution dissolves iodotetronic acid, developing a violet coloration, and producing sodium oximinotetronate; potassium iodide liberates iodine, regenerating tetronic acid. The *silver* salt crystallises from boiling water in small, white needles which are sensitive to light.

*Dichlorotetronic acid*,  $\text{CO}\cdot\text{CH}_2\text{CO}>\text{O}$ ,  
 $\text{CCl}_2\cdot\text{CO}>\text{O}$ , produced when chlorine is passed into chloroform holding iodotetronic acid in suspension, crystallises from petroleum in small needles and melts at  $55-57^\circ$ ; ammonia gives rise to dichloroacetamide.

*Chlorobromotetronic acid*,  $\text{CO}\cdot\text{CH}_2\text{CO}>\text{O}$ ,  
 $\text{C}(\text{HBr})\cdot\text{CO}>\text{O}$ , obtained by the action of chlorine on bromotetronic acid suspended in chloroform, crystallises from a mixture of ether and petroleum in small, colourless needles melting at  $73-74^\circ$ . Concentrated ammonia gives rise to chlorobromoacetamide, which melts at  $125-126^\circ$ .

*Tetronosulphonic acid*,  $\text{SO}_3\text{H} \cdot \overset{\text{OH} \cdot \text{C} \cdot \text{CH}_2}{\underset{\text{C} \cdot \text{CO}}{\text{>O}}}$ , prepared by dissolving tetronic acid in 3 parts of fuming sulphuric acid, crystallises from a mixture of ether and alcohol in flat needles melting at  $83^\circ$ ; it is hygroscopic, and develops a deep red coloration with ferric chloride. The *lead* salt forms needles containing  $2\text{H}_2\text{O}$ , and the *barium* salt contains  $4\text{H}_2\text{O}$ .  
M. O. F.

**Action of Aluminium Chloride on Camphoric Anhydride.** By G. BLANC (*Bull. Soc. Chim.*, 1900, [iii], 23, 693—695).—Observations on the claim to priority put forward by Perkin (*Proc.*, 1900, 16, 18), whose results are considered to furnish fresh proofs of the correctness of the formula assigned by the author to *isolaunonic acid*.  
N. L.

**Action of Zinc on a Mixture of Ethyl Bromoisobutyrate and Ethyl Formate. II. Action of Hydriodic, Hydrobromic, and Sulphuric Acids on  $\beta$ -Hydroxy-*s*-tetramethylglutaric Acid.** By JAKOV I. MICHAILENKO and W. P. JAVORSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 328—346. Compare Abstr., 1899, i, 482).—When  $\beta$ -hydroxy-*s*-tetramethylglutaric acid is heated in sealed tubes with concentrated hydriodic acid at  $130$ — $135^\circ$ , it is reduced, yielding a mixture of lactonic acids in addition to the expected *s*-tetramethylglutaric acid,  $\text{CH}_2(\text{CMe}_2 \cdot \text{CO}_2\text{H})_2$ , which crystallises from hot water in long needles melting at  $185$ — $186^\circ$ ; the *potassium* (with  $2\text{H}_2\text{O}$ ), *barium* (with  $3\text{H}_2\text{O}$ ), *lead* (with  $2\text{H}_2\text{O}$ ), *silver*, *potassium hydrogen*, and *barium hydrogen* (with  $4\text{H}_2\text{O}$ ) salts were prepared. By the action of acetyl chloride on the acid, the corresponding *anhydride*,  $\text{CH}_2 \left\langle \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CMe}_2 \cdot \text{CO} \end{smallmatrix} \right\rangle \text{O}$ , is formed; it separates from ether in long, slender needles melting at  $86$ — $87^\circ$ , and with *p*-toluidine in molecular proportion gives the corresponding *amino-acid*,  $\text{C}_{11}\text{H}_{23}\text{O}_3\text{N}$ , which crystallises from benzene in transparent, yellowish plates melting at  $157$ — $158^\circ$ , slightly soluble in water and readily so in alcohol.

The mixture of lactonic acids also formed during the reduction of the hydroxy-acid with hydriodic acid has a melting point of  $116$ — $120^\circ$ , and after long-continued fractional crystallisation is separated into two monobasic acids, both having the composition  $\text{C}_9\text{H}_{14}\text{O}_4$ . The first of these, melting at  $141$ — $142^\circ$ , forms transparent crystals, and gives a *potassium* salt crystallising from alcohol in transparent plates; the other, which could not be obtained pure, melts at about  $116^\circ$ ; their *barium* salts separate in anhydrous plates. Barium hydrogen salts could not be obtained, and acetyl chloride is without action on the acids. The action of concentrated or dilute sulphuric acid or of hydrobromic acid on  $\beta$ -hydroxy-*s*-tetramethylglutaric acid also yields the same two lactonic acids, but in the case of hydrobromic acid a purer product is formed, the second acid being obtained in opaque aggregates of long crystals melting at  $120$ — $124^\circ$ . That these acids are saturated monobasic acids is shown by their affinity constants, which have the values  $K$  0.00128 (acid melting at  $141$ — $142^\circ$ ) and 0.00150 (acid melting at  $120$ — $124^\circ$ ). On heating these lactonic acids



with potassium hydroxide or barium hydroxide, a dibasic acid is obtained isomeric with the original hydroxy-acid, as is shown by its *barium* salt, which forms fibrous crystals, insoluble in alcohol, and has the composition  $C_9H_{14}O_5Ba \cdot 3H_2O$ ; the free acid could not be prepared, as on decomposing the salts with acid, the lactonic acids are reformed. The two lactonic acids have probably the constitutions:



On oxidising  $\beta$ -hydroxy-*s*-tetramethylglutaric acid with nitrogen oxides, dimethylmalonic and *isobutyric* acids are first formed, the latter being then decomposed with the formation of acetic acid.

T. H. P.

**Researches in the Pyrone Group. VIII. Diethyl Comenate.** By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1900, 30, ii, 16—23).—*Diethyl comenate*,  $OEt \cdot C_5H_3O_2 \cdot CO_2Et$ , obtained by the action of ethyl iodide on the silver derivative of the monoethyl salt, forms acicular, colourless crystals (+  $H_2O$ ), melts at  $79-80^\circ$ , and dissolves in water, alcohol, ether, chloroform, or benzene. When boiled for 3—4 hours with water, it is wholly converted into ethylcomenic acid, which, when hydrolysed by barium hydroxide, yields molecular proportions of acetylcarbonyl ethyl ether and oxalic and formic acids. T. H. P.

[Tartrates of Nickel and Cobalt.] By OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1900, 22, 501—521).—Nickel tartrate was first obtained by Werther (*J. pr. Chem.*, 1844, 32, 400) by saturating a boiling solution of tartaric acid with freshly precipitated nickel hydroxide; his observations are confirmed, except that whilst he considered the salt to be crystalline, the present author regards it as amorphous. Nickel tartrate may also be prepared by the action of tartaric acid on the carbonate. Cobalt tartrate may be similarly obtained by either method; it is precipitated as a pale pink powder, and closely resembles nickel tartrate in its general properties. The potassium nickel tartrate obtained by Fabian (*Annalen*, 1857, 103, 248) by the action of potassium hydrogen tartrate on nickel carbonate was also prepared, but an attempt to produce the corresponding cobalt salt resulted only in the formation of a mixture of the tartrates of cobalt and potassium.

A series of determinations of the depression of the freezing point and of the conductivity of solutions of these nickel and cobalt tartrates yielded results which seem to point to the existence of a polymerised chemical structure.

When potassium hydroxide and nickel tartrate are mixed in molecular proportion, a gelatinous mass is formed which appears to be a hydrated form of potassium nickel tartrate; cobalt tartrate, under the same conditions, yields a flocculent precipitate of variable composition; in each case, the product is soluble in excess of potassium hydroxide. The author concludes from the results of his experiments that these precipitates dissolve in excess of the reagent on account of the formation of a compound in which the nickel or cobalt replaces the hydrogen atoms of the alcoholic hydroxyl groups of tartaric acid. E. G.

**Conversion of Ketones into  $\alpha$ -Diketones.** V. *iso*Propyl *iso*-Butyl Ketone. By GIACOMO PONZIO (*Gazzetta*, 1900, 30, ii, 23—27).—*iso*Propyl *isobutyl* ketone,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , prepared by the action of zinc *isobutyl* on *isobutyryl* chloride, is a mobile liquid boiling at  $147\text{--}148^\circ$  under 744 mm. pressure, and having an agreeable odour resembling that of camphor. The *oxime*,  $\text{C}_8\text{H}_{17}\text{ON}$ , boils unchanged at  $201\text{--}203^\circ$ . On oxidation with nitric acid, the ketone yields *diisopropyl* diketone and dinitro*isobutane*,  $\text{CHMe}_2 \cdot \text{CH}(\text{NO}_2)_2$  (compare Abstr., 1897, i, 317; 1899, i, 111). The *potassium* derivative of dinitro-*isobutane*,  $\text{CHMe}_2 \cdot \text{CK}(\text{NO}_2)_2$ , crystallises from alcohol in sparkling yellow laminae. T. H. P.

**Acetyldioximes of  $\alpha$ -Diketones.** By GIACOMO PONZIO (*Gazzetta*, 1900, 30, ii, 27—30).—The melting point cannot be used as a means of characterising the dioximes of  $\alpha$ -diketones, since these compounds generally melt at about  $170^\circ$ . For this purpose, the best derivatives to use are the diacetyl compounds of the dioximes, which are readily prepared by heating the dioximes with a slight excess of acetic anhydride.

The *diacetyl* derivative of *dimethyl diketoxime*,  $\text{C}_2\text{Me}_2(\text{NOAc})_2$ , separates from alcohol in shining needles which melt at  $112^\circ$  and dissolve in ether, light petroleum, or benzene. The *diacetyl* derivative of *methyl ethyl diketoxime*,  $\text{OAc} \cdot \text{N} : \text{CMe} \cdot \text{CEt} \cdot \text{N} \cdot \text{OAc}$ , crystallises from aqueous alcohol in sparkling prisms which melt at  $68\text{--}69^\circ$ , and are soluble in alcohol, benzene, or light petroleum. The *diacetyl* derivative of *methyl propyl diketoxime*,  $\text{OAc} \cdot \text{N} : \text{CMe} \cdot \text{CPr}^a \cdot \text{N} \cdot \text{OAc}$ , is a dense, colourless liquid decomposing on boiling at the ordinary pressure, that of *methyl isobutyl diketoxime*,  $\text{OAc} \cdot \text{N} : \text{CMe} \cdot \text{C}(\text{N} \cdot \text{OAc}) \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , separates from light petroleum in shining prisms melting at  $42^\circ$ , whilst the *diacetyl* compound of *methyl amyl diketoxime*,

$\text{OAc} \cdot \text{N} : \text{CMe} \cdot \text{C}(\text{NOAc}) \cdot \text{CH}_2 \cdot \text{CH}_2 \text{Pr}^a$ , is a dense oil. The *dibenzyl* derivative of *methyl ethyl diketoxime*,  $\text{CH}_2\text{Ph} \cdot \text{O} \cdot \text{N} : \text{CMe} \cdot \text{CEt} \cdot \text{N} \cdot \text{O} \cdot \text{CH}_2\text{Ph}$ , crystallises from alcohol in white plates melting at  $62\text{--}63^\circ$ . T. H. P.

**Derivatives of Dextrose.** By WILHELM KOENIGS and EDUARD KNORR (*Chem. Centr.*, 1900, ii, 179—180; from *Sitzungsber. Bayr. Akad. Wiss.*, 1900, 103—105).—*Bromotetracetoxydextrose*,  $\text{C}_6\text{H}_7\text{BrO}(\text{OAc})_4$ , prepared by the action of acetyl bromide on grape sugar, melts at  $88\text{--}89^\circ$ , is soluble in light petroleum or ether, but scarcely so in water; it is dextrorotatory and reduces boiling Fehling's solution. By allowing a solution of bromotetracetoxydextrose in methyl alcohol to remain for some time,  $\beta$ -methylglucoside is formed, and by the action of dry silver carbonate or nitrate, tetracetyl- $\beta$ -methylglucoside is obtained. A solution in ethyl alcohol similarly yields corresponding ethyl derivatives. Tetracetylmethylglucoside and tetracetylethylglucoside melt at  $104\text{--}105^\circ$  and at  $105\text{--}106^\circ$  respectively; both are levorotatory, do not reduce Fehling's solution, and are slowly hydrolysed by a cold solution of sodium hydroxide. Pentacetyldextrose, melting at  $130\text{--}131^\circ$ , is formed by shaking silver acetate with a solution of bromotetracetoxydextrose in glacial acetic acid. E. W. W.

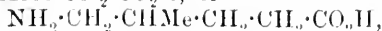
**Nitrocelluloses.** By LÉO VIGNON (*Compt. rend.*, 1900, 131, 509—511).—The nitrocelluloses and nitro-oxycelluloses energetically reduce Pasteur's cupropotassium solution, the reducing power in all cases being independent of the degree of nitration, and equal to about one-fifth that of invert sugar. Since, moreover, it is sensibly the same for both nitrated cellulose and for nitrated oxycellulose, and since cellulose and hydrocellulose are destitute of reducing power, although oxycellulose is strongly reducing (*Abstr.*, 1898, i, 619), it follows that the product of either the partial or complete nitration of cellulose is not a nitrocellulose, but a nitro-oxycellulose. W. A. D.

**Dextrins of Saccharification.** By PAUL PETIT (*Compt. rend.*, 1900, 131, 453—455. Compare *Abstr.*, 1899, i, 559).—The author has investigated the action of diastase on starch paste at 50°, 60°, and 70°, and also on the products of this reaction. The results vary greatly with the age of the diastase and the manner in which it has been kept, and hence the processes have no industrial value. C. H. B.

**Action of Hexamethylenetetramine on the Esters of Chloroacetic and Bromoacetic Acids.** By R. LOCQUIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 660—663).—Hexamethylenetetramine reacts with methyl chloroacetate in chloroform solution to form a *compound*,  $C_6H_{12}N_4 \cdot CH_2Cl \cdot CO_2Me$ , which forms large, colourless crystals melting at 141°. With ethyl bromoacetate, a similar *compound*,  $C_6H_{12}N_4 \cdot CH_2Br \cdot CO_2Et$ , melting at 172—173°, is obtained. When heated with alcoholic hydrobromic acid, this is decomposed with the formation of *ethyl aminooacetate hydrobromide*; this substance, now prepared for the first time, crystallises in long, colourless needles melting at 166°. N. L.

**Terpenes and Ethereal Oils: Ring Disruption among Cyclic Ketones.** By OTTO WALLACH (*Annalen*, 1900, 312, 171—210. Compare this vol., i, 44).—The study of oximes derived from the simplest saturated ketones shows that conversion into an isomeride depends on the transference of nitrogen, in the form of an imino-group, to a position between two carbon atoms of the ring, producing a lactam; the lactam obtained in this way is readily hydrolysed to the corresponding amino-acid, the process affording a convenient means for preparing members of this class. *cyclo*-Pentanoneoxime, for instance, when gently heated with sulphuric acid containing 16 per cent. of water, is converted into 2-piperidone,  $CH_2 \begin{smallmatrix} \diagup CH_2-CO \\ \diagdown CH_2-CH_2 \end{smallmatrix} NH$ , which yields  $\delta$ -aminovaleric acid,  $NH_2 \cdot CH_2 \cdot [CH_2]_2 \cdot CH_2 \cdot CO_2H$ , on hydrolysis.

Sulphuric acid (10 parts: 2 parts of water) converts  $\beta$  methyl*cyclo*-pentanoneoxime (melting at 86°) into the *isooxime*,  $C_6H_{11}ON$ , which crystallises in long needles, melts at 87°, and boils at 147—148° under 15 mm. pressure; it has  $[\alpha]_D +75^\circ$  in water, and forms a white *hydrochloride* which melts at 148—149°. *Aminocaproic acid*,  $NH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CO_2H$ , or



prepared by heating the hydrochloride of the *iso*-oxime with 20 per

cent. hydrochloric acid at  $150^{\circ}$ , melts at  $133\text{--}135^{\circ}$ , and is extremely soluble in water.

*cyclo*-Hexanoneoxime,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C:NOH}$ , is readily converted into the *iso*-oxime,  $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 - \text{CO} \end{smallmatrix} \text{NH}$ , which separates from ether in well-formed crystals melting at  $68\text{--}70^{\circ}$  and boils at  $139^{\circ}$  under 12 mm. pressure; the *hydrochloride* is deliquescent, and melts at  $73\text{--}75^{\circ}$ .  $\epsilon$ -Aminocaproic acid ( $\epsilon$ -*leucine*),  $\text{NH}_2 \cdot \text{CH}_2 \cdot [\text{CH}_2]_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared by heating the *iso*-oxime with hydrochloric acid, crystallises from aqueous solutions to which alcohol has been added, and melts, evolving gas, at  $201\text{--}202^{\circ}$  (compare Gabriel and Maass, Abstr., 1899, i, 595).

$\delta\epsilon$ -Hexenic acid,  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , produced on treating the hydrochloride of  $\epsilon$ -aminocaproic acid with sodium nitrite, melts at  $208\text{--}210^{\circ}$ , and has a sp. gr. 0.962; the refractive index  $n_D$  is 1.4345 at  $23^{\circ}$ , and the molecular refraction, 30.89. The *ammonium* salt is crystalline, and yields the *silver* salt with silver nitrate.

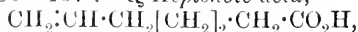
The *isooximes* of methylcyclohexanone (this vol., i, 45) are separated with some difficulty, the  $\alpha$ -modification, which melts at  $105^{\circ}$  and is more sparingly soluble in water than the isomeride, having  $[\alpha]_D - 36.1^{\circ}$  in water; the  $\beta$ -*isooxime* melts at  $68\text{--}69^{\circ}$ , and has  $[\alpha]_D - 22.2^{\circ}$  in water.

[With L. OTTEMANN.]—The *amino*-acid,  $\text{C}_7\text{H}_{15}\text{O}_2\text{N}$ , prepared from the  $\alpha$ -*iso*-oxime, dissolves very readily in water, and melts, evolving gas, at  $187\text{--}188^{\circ}$ ; the *amino*-acid from the  $\beta$ -*isooxime* melts at  $145\text{--}147^{\circ}$ . Both yield the unsaturated *acid*,  $\text{C}_7\text{H}_{12}\text{O}_2$ , which boils at  $220\text{--}225^{\circ}$ .

*Aminodecoic acid*,  $\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}$ , prepared from menthoneisooxime, is scarcely soluble in alcohol and ether, but dissolves in water, from which it separates in well-formed crystals melting at  $194\text{--}195^{\circ}$ ; the *benzoyl* derivative crystallises from methyl alcohol and melts at  $127\text{--}128^{\circ}$ , whilst the *ethyl* ester melts at  $50\text{--}53^{\circ}$  and boils at  $136\text{--}137^{\circ}$  under 12 mm. pressure. Nitrous acid converts it into *decanoic acid*,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , which boils at  $257\text{--}259^{\circ}$  and is identical with menthonic acid (Abstr., 1897, i, 428). It is probable that the aminodecoic acid obtained from menthoneisooxime has the constitution  $\text{NH}_2 \cdot \text{CHPr}^{\beta} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

Tetrahydrocarboxime also yields an *aminodecoic acid*,  $\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}$ , which separates from water in small, transparent crystals melting at  $201\text{--}202^{\circ}$ ; nitrous acid converts it into the corresponding *decanoic acid*,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , which boils at  $257\text{--}260^{\circ}$ , has a sp. gr. 0.936, the refractive index  $n_D$  1.4554 at  $20^{\circ}$ , and a molecular refraction 49.21.

Suberoneisooxime has been described recently (*loc. cit.*); the *aureichloride* is well defined, and melts at  $95\text{--}96.5^{\circ}$ . Hydrolysis converts the *iso*-oxime into  $\xi$ -*amino-n-heptoic* (*aminococanthoic*) acid,  $\text{NH}_2 \cdot \text{CH}_2[\text{CH}_2]_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which crystallises from water, and melts, evolving gas, at  $186\text{--}187^{\circ}$ .  $\xi$ -*Heptenoic acid*,



obtained by the action of nitrous acid on aminoheptoic acid, boils at  $225\text{--}227^{\circ}$ , has a sp. gr. 0.952, the refractive index  $n_D$  1.4425 at  $17^{\circ}$ ,

and a molecular refraction 35.61; the *ammonium* salt is crystalline, and yields the *silver* salt with silver nitrate. Oxidation with potassium permanganate gives rise to adipic acid, the aminoheptoic acid itself yielding pimelic acid.

M. O. F.

**Behaviour and Reactions of Uric Acid and its Salts in Solution.** By HIS, jun., and PAUL (*Chem. Centr.*, 1900, ii, 42; from *Berl. klin. Woch.*, 37, 420).—One part of uric acid dissolves in 88,000 parts of water; it decomposes even in pure aqueous solutions. Both the acid and its salts easily form supersaturated solutions. Colloidal solutions of the urates may also be obtained, and in this state there is no fixed limit to their solubility. From such solutions, the salt soon separates in a very finely divided form, and indeed the properties of the colloidal solutions resemble those of a liquid containing a finely divided solid in suspension rather than those of a true solution. The urates readily separate from solution in an amorphous form, and in this state their solubility is not the same as that of the crystallised salts. Attempts to prepare Rüdel's compound of uric acid and carbamide failed, the presence of carbamide neither affecting the solubility of uric acid nor preventing its precipitation by acids. Metallic salts such as those of potassium or lithium which form easily soluble urates cannot, however, affect the solubility of the acid sodium salt, for being dissociated into ions in solution, the least soluble salt is the first to separate or the last to dissolve. It is therefore impossible to render gouty accretions more soluble by means of potassium or lithium salts.

E. W. W.

**Pentacyano-iron Compounds.** By KARL A. HOFMANN (*Annalen*, 1900, 312, 1—33. Compare Abstr., 1896, i, 517, and Werner, Abstr., 1897, ii, 263).—In accordance with Werner's nomenclature of complex inorganic compounds, the author refers to sodium nitroprusside as *sodium nitrosopentacyanoferrate*, or, preferably, as *ferripentacyanonitrososodium*,  $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_2$ . The substance obtained from it by the action of sodium hydroxide (Abstr., 1896, i, 269), then called quaternary sodium nitroprusside,  $[\text{Fe}(\text{CN})_5\text{NO}_2]\text{Na}_4$ , becomes *sodium nitritopentacyanoferrite* or *ferropentacyanonitritosodium*. Oxidation with potassium permanganate converts this into the deep carmine-red compound,  $[\text{Fe}(\text{CN})_5\text{NO}_2]\text{Na}_3$ , called *sodium nitritopentacyanoferrite* or *ferropentacyanonitritosodium*.

Both sodium nitroprusside and the compound obtained from it by the action of sodium hydroxide readily part with the nitroso-group under the influence of phenylhydrazine, hydroxylamine, aldehyde, and acetone, the same effect being produced by oxidising agents such as potassium hypobromite, lead peroxide, or hydrogen peroxide; sodium prusside,  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]\text{Na}_3$ , is thus produced, and is now called *sodium aquopentacyanoferrite* or *ferropentacyano-aquosodium*. Nitrous acid or bromine water oxidises this to the deep bluish-violet compound,  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]\text{Na}_2$ , *sodium aquopentacyanoferrate* or *ferripentacyano-aquosodium*.

The foregoing five compounds yield *sodium aminopentacyanoferrite* or *ferropentacyano-ammoniosodium*,  $[\text{Fe}(\text{CN})_5\text{NH}_2]\text{Na}_2$ , when treated with ammonia; this was previously called sodium ammonioprusside.

Oxidation with nitrous acid or bromine water converts it into *sodium aminopentacyanoferrate* or *ferripentacyano-ammoniosodium*,  $[\text{Fe}(\text{CN})_5\text{NH}_3]\text{Na}_2$ .

The two first named substances give rise to sodium arseniteprusside,  $[\text{Fe}(\text{CN})_5\text{AsO}_2]\text{Na}_4$ , under the influence of alkaline sodium arsenite; this is termed *sodium arsenitopentacyanoferrite* or *ferropentacyano-arsenitosodium*.

All the compounds mentioned yield sodium sulphiteprusside,  $[\text{Fe}(\text{CN})_5\text{SO}_3]\text{Na}_5$ , when treated with alkaline sodium sulphite (Abstr., 1896, i, 197); this is now called *sodium sulphitopentacyanoferrite*, or *ferropentacyanosulphitosodium*.

The groups or atoms associated with cyanogen in the foregoing nine substances may be replaced by cyanogen, forming sodium ferrocyanide,  $[\text{Fe}(\text{CN})_6]\text{Na}_4$ .

The compound,  $[\text{Fe}(\text{CN})_5\text{NO}\cdot\text{SC}\cdot\text{NH}\cdot\text{NH}_2]\text{Na}_3$ , is obtained by the action of thiocarbamide on sodium nitroprusside.

For experimental details relating to the preparation and identification of these compounds, reference must be made to the original paper.

M. O. F.

**Isomerism in the Aromatic Series.** By WILLIAM OECHSNER DE CONINCK (*Ann. Chim. Phys.*, 1900, [vii], 20, 136—144).—A theoretical paper in which the author cites evidence in favour of the view that two out of the three forms of a di-substitution derivative of benzene are closely related, and differ from the third; the data used include boiling and freezing points, heats of dissolution and formation, and chemical reactivity.

W. A. D.

**Preparation of Iodoso- and Iodoxy-derivatives.** By GIOVANNI ORTOLEVA (*Gazzetta*, 1900, 30, ii, 1—15).—A reply to the criticism of Willgerodt (this vol., i, 339) on the use of pyridine by the author (*Gior. Soc. Sci. Nat. Econ. Palermo*, 23, 1) for the preparation of iodoso- and iodoxy-compounds. A number of compounds have been prepared, the new results being as follows.

*m*-Iodosotoluene,  $\text{C}_7\text{H}_7\text{OI}$ , prepared by the action of water on a pyridine solution of *m*-tolyl iodochloride, forms a yellowish, amorphous mass decomposing and evolving gas at  $180$ — $185^\circ$ ; it is soluble in glacial acetic acid from which the *acetate* is deposited in white needles melting and decomposing at  $147$ — $149^\circ$ .

*m*-Iodoxytoluene is obtained by oxidising a pyridine solution of *m*-iodotoluene with chlorine, and forms a white, flocculent mass exploding violently at  $200^\circ$ ; Bamberger and Hill (this vol., i, 281) gave  $214$ — $221^\circ$ .

1-Iodosonaphthalene, obtained in an impure state by Willgerodt and Schlösser (this vol., i, 283), melts and evolves gas at  $135$ — $145^\circ$ , and forms an acetate melting and decomposing at  $170$ — $175^\circ$ .

1-Iodoxy-naphthalene separates from acetic acid as a gelatinous mass which, when dry, explodes at  $155^\circ$ .

T. H. P.

**Electrolytic Reduction of Nitro compounds.** By FRITZ HABER (*Zeit. angew. Chem.*, 1900, 433—439).—A summary of results previously obtained (this vol., i, 281, 282). It is pointed out that the process of

electrolytic reduction of nitrobenzene is the same as the ordinary chemical reduction process (compare Bamberger, *Abstr.*, 1894, i, 373, 412; 1896, i, 430; 1898, i, 20, 518, 520, 521; this vol., i, 221).

J. C. P.

**Hydrocarbons with High Melting Points from the Last Distillates of Petroleum.** By ROMAN ZALOZIECKI and LUDWIG GANS (*Chem. Zeit.*, 1900, 24, 535—536 and 553—557. Compare Prunier, *Ann. Chim. Phys.*, 1879, [v], 16, 28; Divers and Nakamura, *Trans.*, 1885, 47, 925; Boissieu, *Chem. Zeit.*, 1893, 17, 70; Klaudy and Fink, this vol., i, 284).—The authors have isolated a series of hydrocarbons,  $C_nH_{2n-20}$ , from crude "petrocene," and to this series they give the name *petrocenes*. The melting points of the products obtained are  $250.5^\circ$ ,  $228^\circ$ ,  $221.5^\circ$ ,  $205^\circ$ ,  $191.5^\circ$ ,  $168^\circ$ ,  $155.5^\circ$ ,  $153^\circ$ ,  $147^\circ$ ,  $140^\circ$ ,  $216^\circ$ ,  $230^\circ$ ,  $245$ — $247^\circ$ . The compound melting at  $250.5^\circ$  has the composition  $C_{15}H_{10}$ ; it yields a *picrate* melting at  $178^\circ$ , and a *bromo-derivative*,  $C_{15}H_9Br$ , crystallising from benzene in colourless needles and melting at  $276^\circ$ ; when reduced with sodium and amyl alcohol, it yields a compound,  $C_{15}H_{11}$ , melting at  $177^\circ$ .

The compound,  $C_{16}H_{12}$ , melting at  $221.5^\circ$ , yields a *picrate* melting at  $144^\circ$ , and on reduction gives a *hydrocarbon*,  $C_{16}H_{16}$ , melting at  $185$ — $188^\circ$ . The compound melting at  $205^\circ$  yields a *picrate* which crystallises in ruby-red prisms melting at  $138^\circ$ , and when reduced gives a *hydrocarbon* melting at  $128$ — $130^\circ$ .

When treated with various oxidising agents, the hydrocarbons yield no well-defined products; with fuming nitric acid, they yield yellow *nitro-derivatives*.

The *picrates* are most readily formed in chloroform solution and are readily decomposed by all ordinary solvents. The *petrocenes* are not present in crude petroleum, but are formed during the later stages of distillation, and are found in the petroleum resin (*Harz*). J. J. S.

**Amino-derivatives of Methylphloroglucinol.** By ARTHUR FRIEDL (*Monatsh.*, 1900, 21, 483—497. Compare *Abstr.*, 1894, i, 22).—*Methylphloramine*,  $NH_2 \cdot C_6H_3Me(OH)_2$ , obtained when methylphloroglucinol is treated with ammonia in an atmosphere of hydrogen, crystallises in rosettes of yellowish leaflets, melts at  $149$ — $150^\circ$ , and forms a *triacetyl* derivative, which crystallises in short, colourless needles melting at  $165$ — $166^\circ$ ; the *hydrochloride* crystallises with  $H_2O$  in long, yellowish, monoclinic needles [ $a:b:c=0.9229:1:0.8815$ ;  $a=111.58^\circ$ ], which melt and decompose at  $202^\circ$ . When phloroglucinol is treated with ethylamine, a *diethyldiaminocresol*,  $OH \cdot C_6H_3Me(NHEt)_2$ , is obtained; this melts at  $124$ — $130^\circ$ , and forms a *dihydrochloride* crystallising in clusters of greenish needles which melt and decompose at  $226$ — $228^\circ$ . The *bisdiethylammonium* salt of methylphloroglucinol is obtained by the action of diethylamine on methylphloroglucinol. R. H. P.

**Compounds of Bismuth with Phenols.** By E. RICHARD (*J. Pharm.*, 1900, [vi], 12, 145—148).—On mixing solutions of a bismuth salt and of an orthodihydric phenol, a citron-yellow, insoluble *derivative* of the type  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} Bi(OH)$  is precipitated; such compounds are

decomposed by sulphuric acid into bismuth sulphate and the parent phenol, whilst nitric acid yields oxidation products of the latter. Hydrochloric acid produces a colourless solution, probably containing a chloride of the type  $C_6H_4 \cdot O_2 \cdot BiCl$ , but on diluting this is decomposed to form bismuthyl hydroxide. Compounds were prepared from homocatechol, protocatechuic acid, gallic acid, and methyl gallate, but could not be obtained from meta- or para-dihydric phenols. W. A. D.

**Action of Benzenediazonium Chloride on Alkaline Solutions of Nitrosophenol.** By WALTER BORSCHKE (*Annalen*, 1900, **312**, 211—234. Compare this vol., i, 24).—In view of the synthesis by H. B. Hill (this vol., i, 392) of certain compounds described by the author (this vol., i, 24), a more detailed account of the investigation is published.

5-Nitroso-2-hydroxydiphenyl, 5-amino-2-hydroxydiphenyl, diphenylquinone, 5-nitroso-2-hydroxy-1 : 3-diphenylbenzene, 5-amino-2-hydroxy-1 : 3-diphenylbenzene, 1 : 3-diphenylbenzoquinone, and 2 : 5-dihydroxy-1 : 3-diphenylbenzene have been already described (*loc. cit.*).

2 : 5-Dihydroxydiphenyl,  $C_{12}H_{10}O_2$ , prepared by reducing diphenylquinone with zinc dust and acetic acid, crystallises from dilute alcohol in colourless needles melting at 96—98°. Dianilinophenylbenzoquinone,  $CO < \begin{smallmatrix} C(NHPh) : CPh \\ CH = C(NHPh) \end{smallmatrix} > CO$ , obtained on heating the quinone with alcoholic aniline, crystallises from glacial acetic acid in black needles with bluish-violet lustre, and melts at 195—196°.

5-Nitro-2-hydroxydiphenyl,  $C_{12}H_9O_3N$ , produced on oxidising nitrosohydroxydiphenyl with dilute nitric acid, crystallises from 30 per cent. alcohol in yellow needles, and melts at 126—128°; the benzoyl derivative forms colourless needles, and melts at 120°.

Anilindiphenylbenzoquinone,  $CO < \begin{smallmatrix} C(NHPh) : CPh \\ CH = CPh \end{smallmatrix} > CO$ , prepared from 1 : 3-diphenylbenzoquinone and alcoholic aniline, separates from hot alcohol as a dark red, crystalline powder melting at 167°.

5-Nitroso-2-hydroxy-3-methyldiphenyl,  $C_{13}H_{11}O_2N$ , obtained by the action of benzenediazonium chloride on nitroso-*o*-cresol, crystallises from dilute acetic acid or aqueous alcohol in yellow leaflets; it melts at 170°, and decomposes at 182—183°. The benzoyl derivative crystallises from a mixture of chloroform and alcohol in slender, pale yellow needles, which melt and darken at 170—172°. M. O. F.

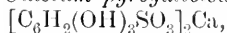
**Diphenylmethyl Oxide.** By VICTOR AUGER (*Bull. Soc. Chim.*, 1900, [iii], **23**, 336—338).—According to Thörner and Zincke (Abstr., 1878, 874), diphenylmethyl oxide [benzhydrol ether], when heated with acetyl chloride, is quantitatively converted into  $\beta$ -benzopinacoline, and must therefore have the composition  $\begin{smallmatrix} CPh_2 : C \\ | \\ CPh_2 : C \end{smallmatrix} > O$ , and not  $O(CHPh_2)_2$ , as generally supposed. The author is unable to confirm this result, which is attributed to impurities in the materials used by Thörner and Zincke. Moreover, the accuracy of the usual formula is proved by the fact that diphenylmethyl oxide is the only product (besides benzhydrol) of the action of water on diphenylmethyl bromide, and that it is obtained in almost theoretical amount



when a solution of the bromide in light petroleum is treated with zinc oxide in the cold. N. L.

**Bromo-derivatives of the Homologous Phloroglucinols.** By JOSEF HERZIG, JACQUES POLLAK, and KARL ROHM (*Monatsh.*, 1900, 21, 498—511. Compare this vol., i, 545).—Dibromomethylphloroglucinol with  $3\text{H}_2\text{O}$  melts at  $112\text{--}115^\circ$ , or when anhydrous at  $132\text{--}134^\circ$  (compare Boehm, Abstr., 1899, i, 32), and yields a *triacetyl* derivative, which melts at  $166^\circ$ . Dimethylphloroglucinol, when treated with bromine in glacial acetic acid solution, forms a *mono-bromo*-derivative, which crystallises in brown needles, and yields a *triacetyl* derivative melting at  $168^\circ$ . Tribromotrimethylphloroglucinol,  $\text{C}_9\text{H}_9\text{O}_3\text{Br}_3$  (compare Boehm, *loc. cit.*), crystallises in monoclinic prisms [ $a:b:c = 0.9911:1:1.5732$ ;  $\alpha = 107^\circ 57'$ ]; it yields trimethylphloroglucinol when reduced with stannous chloride, and triacetyltrimethylphloroglucinol when treated with acetic anhydride. Trimethylphloroglucinol monomethyl ether, when treated with bromine in glacial acetic acid solution at the ordinary temperature, yields tribromotrimethylphloroglucinol. R. H. P.

**Pyrogallolsulphonic Acids.** By MARCEL DELAGE (*Compt. rend.*, 1900, 131, 450—453).—*Calcium pyrogallolsulphonate*,



crystallises with  $4\text{H}_2\text{O}$  in large, rectangular tablets, and with  $5\text{H}_2\text{O}$  in small crystals; both salts are very soluble in water, but are neither deliquescent nor efflorescent. The *barium* salt is a yellowish-white, crystalline powder containing  $2\text{H}_2\text{O}$ ; the *alkali* salts form somewhat large crystals.

The basic calcium salt,  $\text{C}_6\text{H}_2(\text{OH})_2\text{SO}_3\text{Ca}, \text{H}_2\text{O}$ , insoluble in water, is obtained by adding calcium carbonate to a hot solution of pyrogallolsulphonic acid. The acid itself is obtained by the action of sulphuric acid of sp. gr. 1.84 on pyrogallol at about  $100^\circ$ .

C. H. B.

**Occurrence of Methyl Methylantranilate in Oil of Mandarins.** By HEINRICH WALBAUM (*J. pr. Chem.*, 1900, [ii], 62, 135—140).—*Methyl methylantranilate*,  $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , was isolated from 'oil of mandarins' (from the fruit of *Citrus mularensis*, Loureiro) by extracting with 25 per cent. sulphuric acid, as an oil which boiled at  $130\text{--}131^\circ$  under 13 mm. pressure, and when solidified in a freezing mixture melted at  $18.5\text{--}19.5^\circ$ . By heating with alcoholic potash, it was converted into methylantranilic acid (Fortmann, Abstr., 1897, i, 301), and thence into methylaniline by heating with hydrochloric acid under pressure; it was also characterised by conversion into acetyl and dinitro-methylaniline, and nitroso-acetyl- and benzoyl-methylantranilic acids. T. M. L.

**Benzoyl Derivatives of Amino-acids formed by the Fission of Proteids.** By ALBERT SCHULTZE (*Zeit. physiol. Chem.*, 1900, 29, 467—481. Compare Fischer, Abstr., 1899, i, 888, and this vol., i, 172).—The following benzoyl derivatives were obtained from the corresponding amino-acids by the Schotten-Baumann reaction, using

either sodium or potassium hydroxide; as stated by Fischer, however (*loc. cit.*), they are better prepared by substituting sodium hydrogen carbonate for the basic hydroxide.

Benzoylleucine, obtained from natural leucine, crystallises from water in stout, prismatic needles or leaflets, and melts at 135—140° (Fischer gives 126—128°, footnote, *Ber.*, 1899, **32**, 2454); it dissolves in 690 parts of water at 19°, and is inactive in alkaline solution, racemisation probably having occurred in its formation (compare benzoylglutamic acid, *infra*). The *silver*, *lead*, and *zinc* salts crystallise from water, whilst the *potassium* and *barium* salts are very easily soluble in this solvent.

Benzoyl-L-aspartic acid melts at 182—183° (Fischer gives 180—181°), and has  $[\alpha]_D + 34.8^\circ$  in a solution containing 4 mols. of potassium hydroxide (Fischer found  $[\alpha]_D + 37.4^\circ$ ). The *sodium*, *silver*, *copper* (with 2H<sub>2</sub>O), *lead*, and *barium* salts were analysed.

On treating natural, optically active glutamic acid with benzoyl chloride according to the Schotten-Baumann reaction, complete racemisation occurs, and Fischer's racemic benzoylglutamic acid is obtained; the latter, with 1H<sub>2</sub>O, melts at 98°, the anhydrous substance melting at 152—154°, as stated by Fischer. The *silver* and *zinc* salts are crystalline, and the *cadmium* and *lead* salts amorphous; the salts of the alkalis and alkaline earths are very soluble in water.

Dibenzoyltyrosine (compare Fischer, footnote cited) crystallises from dilute alcohol in microscopic needles, melts at 211—212°, and yields microcrystalline *potassium* and *cadmium* salts. W. A. D.

**Synthesis of Hydroxymethyl-*o*-benzoic sulphinide.** By C. MASELLI (*Gazzetta*, 1900, **30**, ii, 31—35).—*Hydroxymethyl-*o*-benzoic sulphinide*,  $C_6H_4 < \begin{smallmatrix} CO \\ SO_2 \end{smallmatrix} > N \cdot CH_2 \cdot OH$ , prepared by heating *o*-benzoic sulphinide with formaldehyde, separates from alcohol in prismatic crystals, which are insoluble in water and melt and partially decompose at 225°. It reduces ammoniacal silver nitrate solution only in presence of potassium hydroxide, and gives no coloration with magenta and sulphuric acid. T. H. P.

**2-Chloro 3-hydroxybenzoic and 2:6 Dichloro-3-hydroxybenzoic Acids.** By GIROLAMO MAZZARA and V. BERTOZZI (*Gazzetta*, 1900, **30**, ii, 84—94).—By the action of sulphuryl chloride on ethyl *m*-hydroxybenzoate, two ethyl chlorohydroxybenzoates are formed, one corresponding with an acid melting at 178°, of the constitution  $[CO_2H : OH : Cl = 1 : 3 : 6]$  and the other with an acid melting at 156—157° (see *Abstr.*, 1899, i, 810); the latter acid is now shown to have the constitution  $[CO_2H : OH : Cl = 1 : 3 : 2]$ .

**2:6-Dichloro-3-hydroxybenzoic acid**,  $C_7H_4O_3Cl_2$ , prepared by the action of sulphuryl chloride on ethyl or methyl 6-chloro-3-hydroxybenzoate or on ethyl 2-chloro 3-hydroxybenzoate, crystallises with 1 mol. H<sub>2</sub>O in very short, doubly-refracting prisms melting at 122—124°; its aqueous solution gives a violet coloration with ferric salts. The *dimethyl* ester,  $C_9H_8O_3Cl_2$ , separates from dilute alcohol in elongated, hexagonal prisms, and from light petroleum in large crystals melting at 57°. The positions of the chlorine atoms in the molecule (one on

either side of the carboxyl radicle) is shown by the fact that the acid cannot be methylated by hydrochloric acid in presence of methyl alcohol.

T. H. P.

**Isomerism of the Formylphenylacetic Esters.** By WILHELM WISLIZENUS (*Annalen*, 1900, 312, 34—64. Compare Abstr., 1896, i, 552).—On applying to the formylphenylacetic esters the method of determining constitution elaborated by Drude (Abstr., 1897, ii, 537), which depends on the absorption of rapidly oscillating electrical vibrations, it is found that the latter are strongly absorbed by the  $\alpha$ -ester, having the enolic structure  $\text{OH}\cdot\text{CH}:\text{CPh}\cdot\text{CO}_2\text{Et}$ ; concurrently with transformation into the  $\beta$ -modification, the absorption decreases, and becomes very slight by the time the liquid has solidified, showing that the  $\alpha$ -ester changes spontaneously into the isomeride.

In the previous paper on this subject, it was stated that both esters yield the same benzoate,  $\text{OBz}\cdot\text{CH}:\text{CPh}\cdot\text{CO}_2\text{Et}$ , which melts at  $87-88^\circ$ . It is now found that by varying the conditions under which this substance is produced, two geometrical isomerides may be obtained.

The  $\alpha$ -benzoate,  $\text{OBz}\cdot\text{CH}:\text{C}(\text{CO}_2\text{Et})\cdot\text{CPh}$ , produced when the sodium derivative of ethyl hydroxymethylenephylacetate is suspended in cooled ether and treated with benzoyl chloride (1 mol.), is a viscous, colourless oil, which boils at  $245-246^\circ$  under 18 mm. pressure, when it becomes converted into the  $\beta$ -benzoate,  $\text{OBz}\cdot\text{CH}:\text{C}(\text{CO}_2\text{Et})\cdot\text{Ph}$ , melting at  $87-88^\circ$ ; the latter has been already described (*loc. cit.*), and is formed when the sodium derivative of the ester is dissolved in water preparatory to treatment with benzoyl chloride. Both modifications yield the dibromide which melts at  $66-67^\circ$ .

The  $\alpha$ -m-nitrobenzoate,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}:\text{C}(\text{CO}_2\text{Et})\cdot\text{CPh}$ , crystallises from ether in monoclinic prisms [ $a:b:c = 1.8752:1:1.9744$ ;  $\beta = 100^\circ 47'$ ], melts at  $101-102^\circ$ , and boils at  $287-288^\circ$  under 23 mm. pressure.

The  $\beta$ -m-nitrobenzoate,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}:\text{C}(\text{CO}_2\text{Et})\cdot\text{Ph}$ , crystallises from ethyl acetate in short, triclinic prisms [ $a:b:c = 1.3842:1:0.6140$ ,  $\alpha = 90^\circ 42'$ ;  $\beta = 112^\circ 34'$ ;  $\gamma = 88^\circ 30'$ ], and melts at  $117-118^\circ$ . Repeated distillation converts the  $\alpha$ -modification into the isomeride, and the same result is achieved when the substance is heated at  $200-220^\circ$  during 1 hour; bromine transforms both isomerides into a vaseline-like substance.

The paper concludes with some remarks on the constitution of metallic derivatives of tautomeric substances; it is suggested that the metallic derivatives of ethyl formylphenylacetate are geometrically isomeric.

M. O. F.

**Synthesis of  $\beta$ -p-isoPropylphenyl- $\alpha$ -methylhydracrylic Acid.** By P. GRIGOROWITSCH (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 324—327).—By acting with zinc and ethyl  $\alpha$ -bromopropionate on cuminaldehyde and saponifying the ester thus formed,  $\beta$ -p-iso-propylphenyl  $\alpha$ -methylhydracrylic acid,  $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , is obtained; it

is almost insoluble in water or benzene, but dissolves in ether or alcohol, and separates from the last-named solvent in the form of hexagonal crystals melting at  $123^{\circ}$ . The *potassium* and *lithium* salts deliquesce in the air; the *sodium* salt (with  $2\frac{1}{2}\text{H}_2\text{O}$ ) crystallises in thin scales; the *barium* salt (with  $4\text{H}_2\text{O}$ ) is soluble in alcohol and slightly so in water, the *calcium* salt (with  $3\frac{1}{2}\text{H}_2\text{O}$ ) having similar properties.

By distilling the acid with sulphuric acid (1 part to 4 of water), *p*-isopropylallylbenzene is obtained, whilst on heating the acid in sealed tubes with hydriodic acid at  $100^{\circ}$  a molecule of water is removed from the molecule and  *$\alpha$ -methyl-p-isopropylcinnamic acid*,  $\text{C}_6\text{H}_4\text{Pr}^{\beta}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ , formed; the latter separates from aqueous alcohol in beautiful, acicular crystals melting at  $90^{\circ}$ . T. H. P.

**Products of Condensation of Dichlorophthalic Anhydride with Diethylaniline.** By ÉMILE SEVERIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 686—693. Compare this vol., i, 296, 450).—3 : 4-Dichloro-2'-diethylaminobenzoylbenzoic acid,  $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$ , obtained by the interaction of 3 : 4-dichlorophthalic anhydride with diethylaniline in the presence of aluminium chloride, crystallises in brilliant scales melting at  $185^{\circ}$ . The *acetate*, or *mixed anhydride*,  $\text{NEt}_2\cdot\text{C}_6\text{H}_4\text{OCl}_2\cdot\text{CO}\cdot\text{OAc}$ , crystallises from boiling benzene or alcohol in colourless scales melting at  $130^{\circ}$ . The *methyl ester*, obtained by the action of sodium methoxide on the preceding compound, crystallises in tufts of slender needles melting at  $152^{\circ}$ , whilst the *ethyl ester* crystallises in yellow needles melting at  $145^{\circ}$ .

The preparation of 3 : 4-dichloro-2'-diethylaminobenzoylbenzoic acid and of the dialkylaminodichloroanthraquinones has already been described (this vol., i, 450). N. L.

***p*-Toluoyle-*p*-benzoic Acid and *pp*-Benzophenonedicarboxylic Acid.** By HEINRICH LIMPRICHT (*Annalen*, 1900, 312, 91—98. Compare Abstr., 1898, i, 322, and this vol., i, 31).—*p*-Toluoyle-*p*-benzoic acid,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , prepared by oxidising *pp*-ditolyl ketone with chromic acid in glacial acetic acid solution, crystallises from alcohol in aggregates of silky leaflets, and melts at  $228^{\circ}$ ; the *barium* and *silver* salts are anhydrous, and the *methyl ester* crystallises in long needles melting at  $126^{\circ}$ . The *chloride* melts at  $110^{\circ}$ , and the *amide* at  $196^{\circ}$ .

*Phenylene ditolyl diketone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , obtained by heating the chloride of the foregoing acid with aluminium chloride in toluene, crystallises from acetone in six-sided, rhombic plates melting at  $188^{\circ}$ .

*Toluoylecarbinoibenzoic acid*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , formed when toluoylebenzoic acid is reduced with zinc dust and ammonia, crystallises from hot water in colourless, triclinic leaflets containing  $\frac{1}{2}\text{H}_2\text{O}$ ; it melts at  $161\cdot5^{\circ}$ , and yields a crystalline *silver salt*.

*Benzophenone-4 : 4'-dicarboxylic acid*,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , produced when oxidising *pp*-ditolyl ketone to *p*-toluyl-*p*-benzoic acid, is separated from the latter in the form of potassium salt; it forms a white, crystalline powder which dissolves with difficulty in alcohol, ether, acetone,

or benzene, and melts above  $360^{\circ}$ . The acid obtained by Zincke and Weber (this Journal, 1875, 155) on oxidising dibenzyltoluene is probably identical with this compound, which has been already described by Ador and Crafts (Abstr., 1878, 405); the *silver* salt is anhydrous, and the *methyl* ester crystallises from acetone in white leaflets and melts at  $224^{\circ}$ . The *chloride* separates from toluene in rhombic crystals melting at  $133^{\circ}$ , and the *amide*, which forms slender, white needles, melts at  $300^{\circ}$ .

*pp-Benzhydrophtallic acid*,  $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , prepared by reducing benzophenone-4:4'-dicarboxylic acid with zinc dust and ammonia, crystallises from water in small, colourless needles, and melts at  $286^{\circ}$ . M. O. F.

*o-Xylylphthaloylic Acid and Phthaloylphthalic Acid.* By HEINRICH LIMPRICHT (*Annalen*, 1900, 312, 99—109).—*o-Xylylphthaloylic\** acid,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , prepared by the action of aluminium chloride on a mixture of phthalic anhydride, *o*-xylene, and carbon disulphide, crystallises from alcohol in aggregates of colourless needles and thin plates melting at  $162^{\circ}$ . The *chloride* melts at  $113$ — $114^{\circ}$ , and the *acetanhydride*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OAc}$ , produced on heating the acid with acetic anhydride, separates from alcohol in monoclinic crystals melting at  $102^{\circ}$ .

*Tolylxylylphthalide*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}_6\text{H}_3\text{Me}_2$ , formed when *o*-xylylphthaloylic chloride is heated with aluminium chloride and toluene in carbon disulphide, is also produced from *p*-toluoyl-*o*-benzoic chloride and *o*-xylene.

*o-Xylylphthalide*,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{C}_6\text{H}_3\text{Me}_2$ , obtained by reducing xylylphthaloylic acid with zinc dust and hydrochloric acid, crystallises from alcohol in small, white needles and melts at  $138^{\circ}$ .

*o-Dimethyl-o-benzylbenzoic acid*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , the final product of reduction of xylylphthaloylic acid, separates from alcohol in highly refractive crystals and melts at  $134^{\circ}$ ; the *silver* salt is amorphous.

*o-Dimethylanthranol*,  $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\rangle\text{C}_6\text{H}_2\text{Me}_2$ , produced by the action of concentrated sulphuric acid on dimethylbenzylbenzoic acid, crystallises from alcohol in small, yellow needles and melts at  $149^{\circ}$ .

*o-Dimethylanthraquinone*,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_2\text{Me}_2$ , an oxidation product of the foregoing substance, sublimes in long, yellow needles melting at  $200^{\circ}$ .

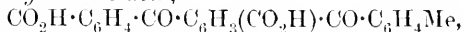
*Phthaloylphthalic acid*,  $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , prepared by oxidising *o*-xylylphthaloylic acid in alkaline solution with potassium permanganate, separates from dilute alcohol in the form of a white, crystalline powder containing  $1\text{H}_2\text{O}$ , and in the anhydrous condition melts at  $189^{\circ}$ . The *ammonium* salt is deliquescent, the *barium* salt

\* The expression *phthaloyl* is employed to represent the group  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$ .

contains  $8\text{H}_2\text{O}$ , and the *silver* salt is anhydrous; the *methyl* ester and the *chloride* are indefinite compounds.

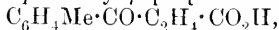
*Phthaloylphthalic anhydride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\rangle\text{O}$ , separates from benzene in crystalline aggregates melting at  $175^\circ$ ; the *imide*, which has perhaps the constitution  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\rangle\text{NH}$ , is obtained by heating ammonium phthaloylphthalate at  $220^\circ$  and melts at  $246^\circ$ .

*Phthaloyltoluylbenzoic acid*,



prepared by heating phthaloylphthalic anhydride with toluene and aluminium chloride, decomposes at  $86^\circ$ , with previously melting; the *silver* and *barium* salts are anhydrous. M. O. F.

*p*-Toluoyl- $\beta$ -propionic Acid. By HEINRICH LIMPRICHT (*Annalen*, 1900, 312, 110—117).—*p*-Toluoyl- $\beta$ -propionic acid,

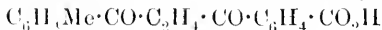


prepared from succinic anhydride and toluene under the influence of aluminium chloride, has been already described by Claus and by Barker; the *methyl* ester forms silky needles and melts at  $43^\circ$ , whilst the *amide* crystallises in white leaflets having a bluish glance, and melts at  $160^\circ$ .

*Tolylpyridazinone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2\\\text{N}—\text{NH}\end{smallmatrix}\rangle\text{CO}$ , prepared by heating the sodium salt of the foregoing acid with aqueous hydrazine (compare Gabriel and Colman, *Abstr.*, 1899, i, 390), crystallises from alcohol and melts at  $147^\circ$ .

*Propiophenonedicarboxylic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_2\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , obtained on oxidising a very dilute, aqueous solution of toluyl- $\beta$ -propionic acid with potassium permanganate, crystallises from hot water, and sinters at  $246^\circ$  without melting definitely; the *barium* and *silver* salts are anhydrous.

*Succitolyl ketone* (*ditolyl ethylene diketone*),  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_3\text{Me})_2$ , one of the products of the action of aluminium chloride on succinic chloride and toluene, crystallises from alcohol in colourless needles and melts at  $161^\circ$ ; oxidation converts it into a mixture of the acids



and  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ .

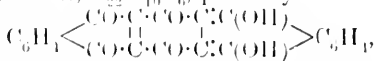
*Ditolylsuccinide*,  $\text{CO}\langle\begin{smallmatrix}\text{C}_2\text{H}_4\\\text{O}\end{smallmatrix}\rangle\text{C}(\text{C}_6\text{H}_4\text{Me})_2$ , produced in association with succitolyl ketone, crystallises from dilute alcohol in lustrous, six-sided leaflets and melts at  $156—157^\circ$ ; the *sodium* and *barium* salts are crystalline. M. O. F.

**Thermal Study of Protocatechuic or 3:4-Dihydroxybenzoic Acid. Influence of Phenolic Hydroxyl.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1900, [iii], 23, 331—333. Compare *Abstr.*, 1899, ii, 353).—Carefully purified protocatechuic acid crystallises in tufts of yellow, prismatic needles melting at  $199^\circ$ . It is neutralised by 1.5 mols. of alkali when phenolphthalein is used as the indicator, whilst with litmus 2 mols. are required. The general acidity is therefore increased

by the presence of the hydroxyl groups, but nevertheless the heats of neutralisation for the first, second, and third equivalents of alkali (12.9, 7.6, and 0.1 Cals. respectively) are somewhat less than the corresponding values for *m*- and *p*-hydroxybenzoic acids which contain one hydroxyl group less. The heat of dissolution of anhydrous protocatechuic acid is -5.82 Cal. The heat of formation of the sodium salt is 17.69 Cal., all the substances concerned being in the solid state, and its heat of dissolution is +0.64 Cal. The former value is practically identical with the heats of formation of the sodium salts of benzoic, *m*-hydroxybenzoic, and *p*-hydroxybenzoic acids, thus confirming the conclusion that the phenolic hydroxyl is without influence on the acidimetric value of the carboxyl group, except when in the ortho-position with respect to the latter. N. L.

**Orthocarboxylic Acids and other Derivatives of 1:2- and 1:4-Dihydroxynaphthalene.** By FRIEDRICH RUSSIG (*J. pr. Chem.*, 1900, [ii], 62, 30—60).—1:4-Dihydroxynaphthalene 2-carboxylic acid, prepared by heating sodium 1:4-dihydroxynaphthalene with carbon dioxide under pressure at 170°, crystallises from dilute alcohol in monoclinic needles, and from acetic acid in monoclinic tablets or prisms containing 1 mol. of acetic acid, and melts at 186° with evolution of carbon dioxide. The *monoacetyl* derivative forms colourless, rhombic plates, and melts at 193° with evolution of gas. The *monomethyl ether*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{OMe}) \cdot \text{CO}_2\text{H}$ , crystallises from acetic acid, melts at 178°, and is converted quantitatively into hydroxymethoxynaphthalene; its *methyl ester*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{OMe}) \cdot \text{CO}_2\text{Me}$ , crystallises from dilute methyl alcohol in hexagonal needles and melts without decomposition at 134°; the *acetyl* derivative,  $\text{OAc} \cdot \text{C}_{10}\text{H}_5(\text{OMe}) \cdot \text{CO}_2\text{H}$ , crystallises from alcohol in felted needles, and melts with decomposition at 172°. The *ethyl ether*,  $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{OEt}) \cdot \text{CO}_2\text{H}$ , crystallises from acetic acid in stout prisms, from alcohol in needles, and melts at 170° with formation of hydroxyethoxynaphthalene; its *ethyl ester* crystallises in hexagonal prisms, and melts at 98°. The acid is converted by stannic chloride into  $\beta$  chloro- $\alpha$ -naphthaquinone, and its constitution is thus established; the methyl and acetyl groups probably enter in the meta position to the carboxyl.

A *condensation product*,  $\text{C}_{22}\text{H}_{10}\text{O}_6$ , probably



in which one naphthalene group has been oxidised from the quinol to the quinone, is formed in the preparation of the acid; it crystallises from aniline in yellow needles, melts above 350°, sublimes without decomposition, and forms an orange coloured sodium salt; the *diacetyl* derivative crystallises from nitrobenzene or xylene in yellow needles, sublimes at about 260°, and melts when quickly heated above 300°. By warming the acid with sulphuric acid, a *condensation product*,  $\text{C}_{22}\text{H}_8\text{O}_6$ , is produced, which crystallises from aniline or nitrobenzene in yellow needles, contains no hydroxyl group, and is regarded as  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{CO} \\ \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{CO} \end{array} \text{C}_6\text{H}_4$ ; sulphonic acids are also produced. By

distilling with zinc dust, the condensation product is reduced to *dinaphthanthracene*,  $C_{22}H_{14}$ , which forms yellowish flakes with a green fluorescence.

*1-Hydroxy-4-methoxynaphthalene* forms long, colourless needles, and melts at  $125^{\circ}$ . *1:4-Dimethoxynaphthalene* crystallises from carbon disulphide in monosymmetric needles, and melts at  $85^{\circ}$ . *1-Hydroxy-4-ethoxynaphthalene* crystallises from water in colourless needles and melts at  $90^{\circ}$ . Methoxynaphthol readily yields an *oxidation product*,  $C_{22}H_{16}O_4$ , which crystallises from pyridine or acetic acid in blue prisms, can be used as a dye in the same way as indigo, and is regarded as  $OMe \cdot C \begin{array}{c} \diagup CH-C-CH \\ \diagdown \end{array} \begin{array}{c} \diagup C-CH \\ \diagdown \end{array} \cdot OMe$ ; the ethyl ether gives a similar compound.

A bye-product in the preparation of the acid, which crystallises in minute, colourless needles and melts at about  $280^{\circ}$ , is regarded as the dicarboxylic acid.

*1:2-Dihydroxynaphthalene-3-carboxylic acid* separates from dilute alcohol in yellow crystals, and melts at  $215^{\circ}$  with evolution of carbon dioxide; the *diacetyl* derivative crystallises from dilute acetic acid in colourless needles and begins to decompose and melt at  $185^{\circ}$ . The *dicarboxylic acid* is produced when the naphthol is heated with carbon dioxide at  $200^{\circ}$ .

T. M. L.

**Double Compounds of Aromatic Aldehydes and Esters with Orthophosphoric Acid.** By P. N. RAIKOW (*Chem. Zeit.*, 1900, 24, 367—368).—Klages has shown (Abstr., 1898, i, 477; 1899, i, 598) that by the action of phosphoric acid on certain aromatic ketones well-crystallised double compounds are produced. The author has obtained similar substances by the combination of phosphoric acid with aromatic aldehydes in which the aldehyde group is directly attached to the benzene nucleus; thus, benzaldehyde and anisaldehyde readily unite with phosphoric acid, whilst formaldehyde, acetaldehyde, valeraldehyde, heptaldehyde, cinnamaldehyde, and cuminaldehyde do not react with it.

If one or both of the hydrogen atoms occupying the *o*-positions in the aldehyde molecule are replaced by radicles, the aldehyde loses its power of combining with phosphoric acid; in this respect, the behaviour of the aldehydes differs from that of the ketones, which only fail to react with phosphoric acid when both the hydrogen atoms in the *o*-position have undergone substitution. If, on the other hand, the hydrogen atom in the *p*-position is replaced, the activity is not affected. Anisaldehyde, for example, unites very readily with phosphoric acid to form a crystalline compound, whilst salicylaldehyde does not combine with it under any conditions.

The ability of aldehydes to react with phosphoric acid is dependent, not only on the position, but also on the chemical nature of the substituting radicles; this is shown by the fact that none of the three isomeric nitrobenzaldehydes combines with this acid, whilst, as previously stated, anisaldehyde does so readily.

Benzoyl chloride and ethyl benzoylacetate do not react with phos-



phoric acid; methyl benzoate combines with it readily to form a colourless, crystalline substance, but the higher esters of benzoic acid and methyl and ethyl salicylates are without action.

By means of experiments with a number of substances which do not contain a carbonyl group, such as benzonitrile, toluonitrile, benzyl chloride and iodide, and benzyl alcohol, the author has proved that the activity of the aldehydes, ketones, and esters towards phosphoric acid is entirely dependent on the carbonyl group which is directly attached to the benzene nucleus. When benzyl alcohol is warmed with phosphoric acid, a stable compound separates as an oil; this is probably a benzyl phosphate. E. G.

**Vanillin in Vinegar-essences.** By AUG. LUDWIG FROBENIUS (*Chem. Zeit.*, 1900, 24, 369).—In a sample of a vinegar-essence, the author has found traces of a terpene, and also a substance which yields vanillin on oxidation and is probably coniferin (compare Stocký, this vol., ii, 454). E. G.

**Synthesis of Benzene by the Action of Zinc Ethyl on Acetophenone.** By MAURICE DELACRE (*Chem. Centr.*, 1900, ii, 255; from *Bull. Acad. roy. Belg.*, 1900, [iii], 39, 64—68. Compare *ibid.*, 1896, [iii], 32, 446).—From the alcoholic mother liquors of  $\alpha$ -homodypnopinacone, in addition to  $\gamma$ -dypnopinacolin,  $\gamma$ -homodypnopinacone,  $C_{32}H_{28}O_2$ , has also been isolated. It crystallises from glacial acetic acid in lustrous, heavy needles, melts at  $205^\circ$ , is not attacked by prolonged boiling with glacial acetic acid, but when boiled with acetyl chloride forms nodules and silky needles of a substance which melts at  $146^\circ$  ( $\alpha$ -homodypnopinacolin). A diagram is given showing the compounds formed in the conversion of acetophenone into triphenylbenzene. E. W. W.

**Gradual Synthesis of the Benzene Ring.** By MAURICE DELACRE (*Chem. Centr.*, 1900, ii, 255—256; from *Bull. Acad. roy. Belg.*, 1900, [iii], 39, 68—87).—From a determination of the quantity of zinc ethyl which is required to convert dypnone into dypnopinalcolene,  $C_{32}H_{26}$ , it is evident that dypnone is first polymerised to dypnopinacone before forming the hydrocarbon, and that in the first change the zinc ethyl does not act as a reducing agent. Similarly, in the synthetical formation of triphenylbenzene from acetophenone, dypnone undergoes a like polymerisation. The reverse change is also easily effected, for by distilling dypnopinacone under 20 mm. pressure a good yield of almost pure dypnone boiling at  $270^\circ$  is obtained. Moreover, Gesché has found (compare following abstract) that by the action of alcoholic potash on dypnone, dypnopinacone is formed, and that this is then easily decomposed into  $\alpha$ -dypnopinacolin. Polymerisation is also brought about by heating dypnone with potassium cyanide at  $160^\circ$ , although there is no action at  $110^\circ$ .

From the products obtained by heating dypnone for 8 days at  $225$ — $230^\circ$ , not only ethylbenzene, but also the polymeride of allylbenzene boiling at above  $320^\circ$  has been isolated (compare Errera, *Gazzetta*, 1884, 14, 504). When dry dypnopinalcolene,  $C_{32}H_{26}$ , is distilled, triphenylbenzene and a hydrocarbon boiling at about  $340^\circ$  are formed. The latter is probably identical with that obtained from dypnone.

The formation of reduction products such as dypnopinacolin alcohol,  $C_{32}H_{28}O$ , and dypnopinalcolene,  $C_{32}H_{26}$ , in the distillation of dypnone is accompanied also by simultaneous oxidation, benzoic acid and diphenyl-furfuraldehyde being formed.

E. W. W.

**Action of Potassium Hydroxide on Dypnone.** By Louis GEsCHÉ (*Chem. Centr.*, 1900, ii, 256—257; from *Bull. Acad. roy. Belg.*, 1900, 293—313).—By heating dypnone with alcoholic potash in a sealed tube, triphenylbenzene is formed, but this is really the result of secondary reactions, for if the mixture be heated in an open flask at  $180^\circ$ , benzoic acid and a hydrocarbon,  $C_{25}H_{22}$ , are the final products. The action takes place in three phases. The dypnopinacone first formed is converted into  $\alpha$ -isodypnopinacolin,  $C_{32}H_{26}O$ , by elimination of water, and this is finally decomposed by the action of the alkali, forming benzoate and the hydrocarbon. The hydrocarbon,  $C_{25}H_{22}$ , crystallises in white leaflets, becomes greenish on exposure to light, melts at  $95^\circ$ , is soluble in alcohol, and when reduced with sodium amalgam yields the hydrocarbon  $C_{25}H_{24}$ , which separates in large crystals and melts at  $144^\circ$ .  $\alpha$ -isodypnopinacolin,  $C_{32}H_{26}O$ , prepared by the action of alcoholic potash on dypnone at the ordinary temperature, crystallises from glacial acetic acid or hot alcohol, and melts at  $131.5$ — $132^\circ$ . Since  $\alpha$ -homodypnopinacolin, melting at  $130^\circ$ , was isolated, homodypnopinacone is probably also a product of the action of alcoholic potash at the ordinary temperature. Dypnopinacone,  $C_{32}N_{22}O_2$ , obtained by the action of the alkali on dypnone for 3 hours, crystallises from ether and alcohol in white needles and melts at  $162^\circ$ ; when dissolved in hot glacial acetic acid, it forms isodypnopinacolin.

E. W. W.

**Isomerism in the Menthol Series. III.** By IWAN L. KONDAKOFF and E. LUTSCHININ (*J. pr. Chem.*, 1900, [ii], 62, 1—30. Compare this vol. i, 104).—The variations in the physical constants of fenchyl alcohol are probably due to partial racemisation, and this view has been confirmed by the isolation, from the crude reduction-product of *d* fenchone, of a liquid which solidifies on cooling, boils at  $199^\circ$  (fenchyl alcohol boils at  $201^\circ$ ), and is feebly dextrorotatory. The action of phosphorus pentachloride on fenchyl alcohol gives an impure chloride containing fenchene; a much purer product is obtained by heating the alcohol on a water-bath with concentrated hydrochloric acid; at higher temperatures, a *dichloride* is produced, in which the diagonal bond is probably broken. By the action of alcoholic potash on the chloride at  $100^\circ$ , there is produced along with the fenchene a *secondary fenchyl chloride*,  $C_{10}H_{17}Cl$ , which crystallises from alcohol, melts at  $79$ — $80^\circ$ , has  $[\alpha]_D + 16.33'$ , does not react with moist silver oxide, and resembles bornyl chloride in its odour and other properties; at  $150^\circ$ , only fenchene is produced. Crude fenchyl chloride appears, therefore, to be a mixture of the solid secondary chloride with a much larger amount of a tertiary chloride, probably liquid, which is much more easily decomposed by alcoholic potash, and is formed as the result of an isomeric change similar to that which takes place in the case of menthol and carvomenthol (Kondakoff and Lutschinin, *loc. cit.*). Fenchene hydrochloride closely resembles fenchyl chloride, and is probably almost all tertiary;

moist silver oxide converts it into Bertram and Helle's *isofenchyl* alcohol (this vol., i, 398).

*Fenchyl bromide*, prepared by the action of cold hydrobromic acid on *l*-fenchyl alcohol from *d*-fenchone, boils at 92–96° under 11 mm. pressure, has a sp. gr. 1.2368 at 19.5°/19.5°,  $n_D$  1.4988,  $[\alpha]_D - 43.17'$ . A small amount of a *dibromide* is also produced, which crystallises from alcohol and melts at 49°. *Fenchene hydrobromide* resembles fenchene bromide, but gave  $[\alpha]_D - 27.16'$ .

By the action of alcoholic potash on fenchyl bromide, and to a less extent on the chloride, a fenchene of low boiling point is produced, and it is suggested that the product contains at least two isomerides.

T. M. L.

**Sesquiterpene of Oil of Ginger.** By HUGO VON SODEN and WILHELM ROJAHN (*Chem. Centr.*, 1900, ii, 97; from *Pharm. Zeit.*, 45, 414–415).—The sesquiterpene, *zingiberene*,  $C_{15}H_{24}$ , which is the main constituent of oil of ginger, is a colourless, almost odourless oil easily soluble in ether, light petroleum, benzene, or absolute alcohol; it boils at 269–270°, or at 134° under 14 mm. pressure, has a sp. gr. 0.872 at 15° and a rotatory power of  $-69^\circ$  (100 mm. tube). The hydrogen chloride and hydrogen bromide additive compounds and the tetrabromide are liquids. It forms neither a nitrosochloride nor a nitrosate.

The lower fractions of oil of ginger contain small quantities of aldehyde-like substances (fatty aldehydes?).

E. W. W.

**Natural Resins [Ueberwallungsharze]. VI. Dry Distillation of Lariciresinol.** By MAX BAMBERGER and EMIL VISCHNER (*Monatsh.*, 1900, 21, 564–570. Compare Abstr., 1899, i, 929).—Lariciresinol, when subjected to dry distillation, yields guaiacol, pyroguaiacin, and an undetermined compound melting at 140°, together with carbon dioxide and gaseous hydrocarbons.

R. H. P.

**Constitution of  $\beta$ -isoCinchonine.** By ZDENKO HANNS SKRAUP [and in part H. COPOLY and G. MEDANICH] (*Monatsh.*, 1900, 21, 512–534. Compare Abstr., 1899, i, 960).— $\beta$ -isoCinchonine, when treated with hydrogen bromide, yields hydrobromocinchonine, does not react with phenylhydrazine, and, when treated with methyl iodide, yields a methiodide which melts at 232.5° (not 253° as given by Jungfleisch and Léger, Abstr., 1888, i, 380). By treatment of  $\beta$ -isocinchonine hydriodide with methyl iodide, an isomeric *methiodide*, which is an unstable oil, is obtained, thus showing that  $\beta$ -isocinchonine, like cinchonine, is a double tertiary base.  $\beta$ -isocinchonine acid sulphate, which crystallises with  $4\frac{1}{2}H_2O$  (not  $4H_2O$ , compare Hesse, Abstr., 1891, i, 584), when heated at 110°, is transformed into  $\beta$ -iso $\psi$ -cinchonine,  $C_{19}H_{22}ON_2$ , which is not of ketonic character like the analogous cinchonine (cinchotoxine) obtained by heating cinchonine acid sulphate. When oxidised with chromic acid,  $\beta$ -isocinchonine yields carbon dioxide, formic and cinchonic acids, and  $\beta$ -isomerocinchonine [ $\beta$ -isomerocinchonine],  $C_{19}H_{15}O_2N$ , an amorphous optically active base isomeric with meroquinine, which is obtained from cinchonine in a similar manner

(Koenigs, Abstr., 1894, i, 392). These reactions show that the quinoline portion of the cinchonine molecule is not affected when it is transformed to  $\beta$ -isocinchonine.

The following new compounds and properties are described:  $\beta$ -isocinchonine hydrochloride dissolves in about 50 parts of water, the hydriodide crystallises with  $\text{H}_2\text{O}$  in needles, and melts at  $217^\circ$ ; hydrobromocinchonine dissolves in 250—270 parts of absolute alcohol, and its dihydrobromide in about 60 parts of water; the *hydriodide*,  $\text{C}_{19}\text{H}_{22}\text{ON}_2\cdot\text{MeI}\cdot\text{HI}$ , of the unstable, oily  $\beta$ -isocinchonine methiodide, which crystallises in yellow needles, turns dark red when heated, sinters at  $190^\circ$ , and melts at  $196^\circ$ ;  $\beta$ -iso- $\psi$ -cinchonine hydrochloride,  $\text{C}_{19}\text{H}_{22}\text{ON}_2\cdot\text{HCl}$ , which forms compact crystals, with  $3\text{H}_2\text{O}$ , and is soluble in 2 parts of water; the *hydriodide*, which crystallises in prisms, with  $2\text{H}_2\text{O}$ , and is slightly soluble in water; the *dihydriodide*, which crystallises in yellow prisms, with  $3\text{H}_2\text{O}$ , melts at  $163.5$ — $165^\circ$ , and is easily soluble in water;  $\beta$ -isomeroquinine aurichloride,  $\text{C}_{19}\text{H}_{15}\text{O}_2\text{N}\cdot\text{HAuCl}_4$ , which crystallises in prisms, melts and decomposes at about  $180^\circ$ .

R. H. P.

$\alpha$ - and  $\beta$ -Isocinchonine. By ZDENKO H. SKRAUP and RUD. ZWERGER (*Monatsh.*, 1900, 21, 535—563. Compare preceding abstract and Abstr., 1899, i, 960).— $\alpha$ - and  $\beta$ -isocinchonine resemble cinchonine in that their acid sulphates undergo molecular transformation when heated; thus  $\beta$ -isocinchonine sulphate yields  $\beta$ -iso- $\psi$ -cinchonine (*loc. cit.*), and  $\alpha$ -isocinchonine sulphate yields two isomeric bases, namely,  $\alpha$ -isocinchonine, which is of a ketonic nature, and  $\alpha$ -iso- $\psi$ -cinchonine, which is an amorphous substance melting at  $73$ — $74^\circ$  and does not react with phenylhydrazine. Neither  $\alpha$ -isocinchonine nor  $\beta$ -isocinchonine react with phosphorus pentachloride, acetic anhydride, benzoyl chloride, phenylcarbimide, or phenylhydrazine.  $\alpha$ -isocinchonine, like  $\beta$ -isocinchonine (*loc. cit.*), when oxidised with chromic acid, yields cinchonine acid and a substance (not yet investigated) resembling meroquinine (Koenigs, Abstr., 1894, i, 392).

The following new compounds and properties are described:  $\alpha$ -isocinchonine dissolves in 70 parts of light petroleum, the hydrochloride crystallises with  $3\text{H}_2\text{O}$  (not  $2\text{H}_2\text{O}$  as previously described, *loc. cit.*), and the acid sulphate crystallises with  $3\frac{1}{2}\text{H}_2\text{O}$  in needles; hydriodo-cinchonine dissolves in 57 parts of absolute alcohol, and its dihydriodide in about 11 parts of 50 per cent. alcohol; *allocinchonine* sulphate dissolves in 120 parts of water at  $21^\circ$ ; cinchonine chloride crystallises with  $2\text{H}_2\text{O}$ , melts at  $82^\circ$ , but when anhydrous at  $72^\circ$ , and has a specific rotation  $[\alpha]_D +48.77^\circ$ ; its *hydrochloride*,  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{Cl}\cdot\text{HCl}$ , crystallises in white, matted needles, which melt at  $213$ — $214^\circ$ ; cinchonine dissolves in 70 parts of toluene, in 150 parts of a mixture of equal parts of toluene and chloroform, and in 200 parts of a similar mixture of benzene and chloroform; *cinchoninephenylurethane* crystallises in tablets and melts at  $198^\circ$ ;  $\alpha$ -isocinchoninephenylhydrazine melts and decomposes at  $108$ — $109^\circ$ ;  $\alpha$ -iso- $\psi$ -cinchonine hydriodide,  $\text{C}_{19}\text{H}_{22}\text{ON}_2\cdot\text{HI}\cdot\text{H}_2\text{O}$ , crystallises in prismatic tables, and when anhydrous melts at  $235$ — $236^\circ$ ; the *ovalate*,  $(\text{C}_{19}\text{H}_{22}\text{ON}_2)_2\cdot\text{H}_2\text{C}_2\text{O}_4\cdot 6\text{H}_2\text{O}$ , crystallises in flakes.

R. H. P.

**Oxidation Products of Cotarnine.** By G. F. WULFF (*Bull. Acad. St. Petersb.*, 1899, [v], 11, 45—57).—When cotarnine is oxidised in alkaline solution with potassium permanganate, the principal products are oxycotarnine, cotarmethylimine, and carbon dioxide, small quantities of potassium cotarnate and oxalate being also formed.

*Oxycotarnine*,  $\text{CH}_2 \begin{array}{c} \text{O} \cdot \text{C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{CO} \cdot \text{NMe} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{O} \cdot \text{C} \cdot \text{C}(\text{OMe}) \cdot \text{CH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , crystallises from water in colourless prisms containing  $1\text{H}_2\text{O}$ , and melting at  $69\text{--}70^\circ$ ; at  $50\text{--}90^\circ$ , the water is expelled, the anhydrous compound obtained having a melting point of  $108^\circ$ . It is slightly soluble in light petroleum, more so in ether, and readily in alcohol, chloroform, benzene, or water; it is precipitated from its aqueous solution by strong potassium hydroxide solution, and is not changed on boiling with concentrated hydrochloric acid. It dissolves readily in concentrated sulphuric acid, and on warming the solution assumes a purple colour, whilst if the cooled liquid is mixed with a few drops of water, it becomes violet. It does not form an acetyl compound, but yields a *bromo*-derivative,  $\text{C}_{12}\text{H}_{12}\text{O}_4\text{NBr}$ , which is deposited as a white, crystalline precipitate, gradually changing to slender, silvery needles which are soluble in water and melt at  $125\text{--}126^\circ$ . The *aurichloride* forms a slightly soluble, yellow, crystalline precipitate, melting and decomposing at  $160^\circ$ , and the *platinichloride*,  $(\text{C}_{12}\text{H}_{13}\text{O}_4\text{N})_2\text{H}_2\text{PtCl}_6$ , separates in rectangular, orange plates, which darken at  $100^\circ$ , and melt and decompose at  $179\text{--}180^\circ$ .

*Cotarmethylimine*,  $\text{CH}_2 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}_6\text{H}(\text{OMe}) \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{NMe}$ , crystallises from alcohol or a mixture of alcohol and chloroform in slender, white, fibrous needles, which sublime at  $190\text{--}195^\circ$ , and melt and decompose at  $205\text{--}206^\circ$ ; it is only slightly soluble in water, but dissolves readily in concentrated sulphuric acid, forming a yellowish-orange liquid. When heated with potassium hydroxide solution, it yields methylamine and cotarnic acid.

T. H. P.

**Cytisine and its Alkyl Derivatives.** By A. RAUWERDA (*Chem. Centr.*, 1900, ii, 268—269; from *Ned. Tijds. Pharm.*, 12, 161—173).—Cytisine distils at  $218^\circ$  under a pressure of 2 mm., forming a colourless liquid, which afterwards solidifies, and a sublimate consisting of slender needles. It separates from alcohol in rhombic crystals, and when treated with nitrobenzene containing dinitrothiophen it gives a rather stable, reddish-violet coloration; with coniine, it forms a similar, but much more evanescent, coloration. Data regarding the solubility of cytisine in chloroform, methyl alcohol, ethyl alcohol, benzene, acetone, and ethyl acetate at various temperatures are quoted. The rotatory power of cytisine in 15 per cent. aqueous solution at  $12^\circ$  is  $[\alpha]_D - 127.40'$ , and this constant increases to a concentration of 20 per cent. and then again decreases. The original paper contains copious data in reference to the rotatory power in various solvents. *Methylcytisine*, prepared by heating cytisine with a slight excess of methyl iodide at  $100^\circ$ , crystallises from alcohol in long columns, and from water in plates. It is easily soluble in water, chloroform, methyl alcohol, ethyl alcohol, benzene, or acetone. The rotatory power in 10

per cent. aqueous solution is  $[\alpha]_D - 234^{\circ}10'$ , and attains a maximum at a concentration of about 25 per cent. *Ethyleclysine* was obtained only as a syrup. *Cetyleclysine* crystallises from alcohol in slender, white needles, melts at  $55-56^{\circ}$ , is readily soluble in alcohol, methyl alcohol, or chloroform, and insoluble in water; in 5 per cent. chloroform solution at  $8^{\circ}$ , the rotatory power is  $[\alpha]_D - 112^{\circ}$ . E. W. W.

**Crystalline Form of Histidine Dichloride.** By ARTHUR SCHWANTKE (*Zeit. physiol. Chem.*, 1900, 29, 493).—Histidine dichloride [orthorhombic,  $a:b:c = 0.76537:1:1.77516$ ] is apparently isomorphous with histidine monochloride [ $a:b:c = 0.76665:1:1.71104$ ]; since the latter contains  $11H_2O$ , whilst the former is anhydrous, the second mol. of hydrogen chloride in the dichloride appears to fulfil the same function as the water of crystallisation of the monochloride.

W. A. D.

**Tetramethyldiaminodiphenylmethane and similar Substances.** By GEORG COHN (*Chem. Zeit.*, 1900, 24, 564. Compare Abstr., 1895, i, 98).—Tetramethyldiaminodiphenylmethane is most readily obtained when 16 parts of dimethylaniline, 6 of formaldehyde solution (40 per cent.), and 20 of hydrochloric acid (25 per cent.) are heated for several hours on the water-bath. A smaller amount of acid may be employed or else zinc chloride. Diphenylmethane derivatives cannot be obtained from dimethyl-*o*-toluidine. Both diethylaniline and methyldiphenylamine, however, readily enter into condensation; in the latter case, the reaction is violent, and it is necessary to employ acetic in place of hydrochloric acid. The product is a yellowish-white powder insoluble in the ordinary solvents, and when oxidised with dichromate in the presence of acetic and hydrochloric acid yields blue or green dyes. J. J. S.

**Direct Synthesis of Ketodihydroquinazolines from Ortho-amino-acids.** By MARSTON TAYLOR BOGERT and AUGUST HENRY GOTTHELF (*J. Amer. Chem. Soc.*, 1900, 22, 522—535. Compare this vol., i, 412).—When anthranilic acid (1 mol.) and acetonitrile (2—3 mols.) are heated together in a sealed tube for 6 hours at  $200-210^{\circ}$ , 2-methyl-4 ketodihydroquinazoline is formed, identical with that obtained by Weddige (Abstr., 1885, 661; 1887, 1044), by Bischler and Burkart (Abstr., 1893, i, 530), and by Niementowski (Abstr., 1895, i, 571), carbon dioxide and acetanilide being also produced. The yield of the quinazoline is increased by the addition of acetic anhydride; neither acetic anhydride nor acetyl chloride react with it under ordinary conditions. The same compound also results from the action of acetonitrile on acetylanthranilic acid, and of acetic anhydride on acetylanthranilic nitrile.

The authors have repeated the method of preparation described by Niementowski (*loc. cit.*), and, in addition to 2-methyl-4-ketodihydroquinazoline, have obtained acetanilide, and a substance which crystallises in needles, melts at  $194-195^{\circ}$ , and yields the quinazoline when boiled with hydrochloric acid, or on sublimation.

A number of salts of the quinazoline were prepared and found to possess generally the characters ascribed to them by Niementowski

(Abstr., 1896, i, 578). The methyl ether melts at  $72^{\circ}$ , or, when anhydrous, at  $111^{\circ}$ , and is therefore identical with the  $\beta$ -dimethyl- $\Delta\psi$ -oxyquinazolino of Weddige (Abstr., 1887, 1044).

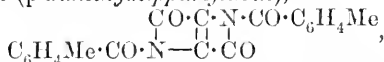
It has been stated by Bedson (Trans., 1880, 37, 756) that, by the action of acetic anhydride on anthranilic acid, diacetyl-anthranilic acid is formed; the present authors, however, could not obtain this compound, but only the monoacetyl derivative. E. G.

**Constitution of Hippuroflavin.** By LEOPOLD RÜGHEIMER (*Annalen*, 1900, 312, 81—90).—A discussion of the respective claims of the formulæ advocated by the author and by Erlenmeyer, jun.

M. O. F.

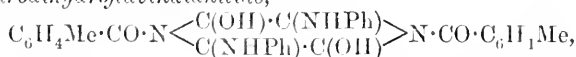
**Homologues of Hippuroflavin.** By LEOPOLD RÜGHEIMER and F. FEHLHABER (*Annalen*, 1900, 312, 65—80. Compare Abstr., 1896, i, 61).—*Ethyl p-tolurate*,  $C_6H_4Me \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$ , dissolves very readily in alcohol, ether, benzene, or chloroform, but more sparingly in petroleum, from which it crystallises in long needles melting at  $69^{\circ}$ .

*p-Toluroflavin* (*p*-dimethylhippuroflavin),



obtained by the action of phosphorus pentachloride on ethyl tolurate (compare Abstr., 1894, i, 55), is insoluble in ether, benzene, chloroform, or petroleum, and almost insoluble in alcohol; it crystallises from hot glacial acetic acid in aggregates of small, yellow needles, and becomes brown when heated, but does not melt at  $285^{\circ}$ .

*p-Tolurodihydroflavindi-anilide*,

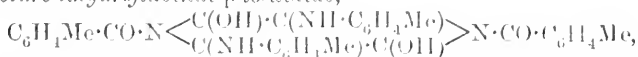


produced when *p*-toluroflavin is heated with aniline (2 mols.) and glacial acetic acid, is insoluble in common solvents; the solution in alcoholic potash is yellow.

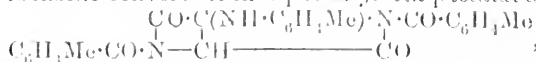
*p-Toluroflavinanilide*,  $C_6H_4Me \cdot CO \cdot N \begin{array}{c} CO \cdot C(NHPh) \cdot N \cdot CO \cdot C_6H_4Me \\ | \quad | \\ CH \text{ ————— } CO \end{array}$ ,

formed on heating tolurodihydroflavindi-anilide with nitrobenzene in a reflux apparatus during 30 minutes, crystallises from alcohol in small, yellow, silky needles, and melts at  $255$ — $257^{\circ}$ , when it decomposes.

*p-Tolurodihydroflavindi-p-toluidide*,



prepared from *p*-toluroflavin and *p*-toluidine, does not melt at  $270^{\circ}$ ; boiling nitrobenzene converts it into *p-toluroflavin-p-toluidide*,



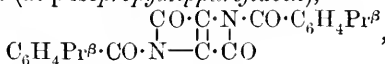
which crystallises from alcohol in small, golden, lustrous needles which remain unfused at  $270^{\circ}$ .

*Ethyl o-tolurate*,  $C_6H_4Me \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$ , crystallises from water in needles and melts at  $55^{\circ}$ .

*o-Toluroflavin* (*o*-dimethylhippuroflavin),  $C_{20}H_{11}O_4N_2$ , crystallises from hot alcohol in small, yellow needles which darken when heated; it does not melt at  $285^{\circ}$ .

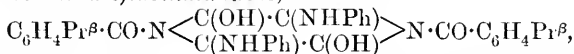
*Ethyl cuminarate*,  $C_6H_4Pr^{\beta} \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$ , crystallises from ether in small needles and melts at  $49^{\circ}$ .

*Cuminuroflavin* (*di-p-isopropylhippuroflavin*),

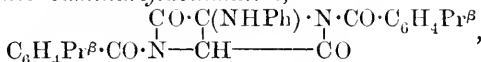


crystallises from alcohol and from acetic acid in thin plates with golden lustre and melts at  $230-235^{\circ}$ , when it decomposes.

*Dihydrocuminuroflavindianilide*,



is very sparingly soluble in common solvents; boiling nitrobenzene converts it into *cuminuroflavinanilide*,



which crystallises from amyl alcohol in pale yellow, silky needles and does not melt at  $290^{\circ}$ .

*2:4:5-Trimethylhippuric (duryluric) acid*,



crystallises from water in large, lustrous plates or in stellate aggregates of needles and melts at  $167^{\circ}$ ; the *calcium*, *barium*, and *zinc* salts contain  $3H_2O$ ,  $4H_2O$ , and  $2\frac{1}{2}H_2O$  respectively. The *ethyl* ester crystallises in small needles and melts at  $96^{\circ}$ . M. O. F.

**Derivation and Rational Nomenclature of the Quinopyridines.** By CONRAD WILLGERODT (*Chem. Zeit.*, 1900, 24, 437—439).—This paper consists of a discussion of the constitution and nomenclature of the 28 possible isomeric quinopyridines. E. G.

**Formation of Safranines.** By D. A. CHARDIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 309—324).—The formation of safranines by the oxidation of 1 mol. of a *p*-diamine with 2 mols. of a primary monoamine is influenced by the number and position of the methyl groups of the monoamine, and the author's experiments in this direction lead to the following conclusions. When the monoamine has only one methyl group in the molecule, the relative position of the methyl and amino-groups has no influence on the formation of safranines, which can thus be obtained with *o*-, *m*-, or *p*-toluidine. When two or more methyl groups are present in the molecule of the monoamine, for the formation of a safranine, it is necessary that one of them should be in the *p*-position to the amino-group, and that the others can be divided into pairs of groups in the *p*-position to one another; if the number of methyl groups be even, the remaining one may occupy any position.

The preparation of safranines by the oxidation of a monoamine in presence of nitrosodimethylaniline hydrochloride can be explained according to two different schemes of condensation, between which the facts are insufficient to admit of a decision being formed. T. H. P.

**Reduction of Aromatic Aldazines.** Synthesis of Benzylhydrazine. By THEODOR CURTIUS [in part with E. HAAGER, E. HARDING, A. PROPPE, and G. SPRENGER] (*J. pr. Chem.*, 1900, [ii], 62, 83—126).—The substance prepared by Curtius and Quedenfeldt



(Abstr., 1899, i, 276) by reducing benzaldazine with sodium amalgam is *benzylbenzylidenehydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$ , and not *dibenzylhydrazine*, as was previously supposed; the *hydrochloride*, *picrate*, *acetyl*, *benzoyl*, and *nitroso*-derivatives are also hydrazones, and the oxidation product is not 'bis-azidiphenylmethane,' but *dibenzylidibenzylidenehydrotetrazone*,  $\text{N}_2(\text{CH}_2\text{Ph})_2(\text{N}:\text{CHPh})_2$ . *s*-Dibenzylhydrazine is, however, also formed in the reduction: the *hydrochloride* forms glistening flakes, only slightly soluble in cold water, and melts at  $225^\circ$ ; the *base* crystallises from dilute alcohol, melts at about  $47^\circ$ , and readily decomposes; the *diacetyl* derivative crystallises from alcohol in prisms and melts at  $117\text{--}118^\circ$ ; the *dibenzoyl* derivative crystallises from alcohol in minute needles and melts at  $164^\circ$ ; the *dinitroso*-derivative forms pale yellow crystals and melts at  $35\text{--}40^\circ$ ; when crystallised from alcohol or heated at  $30\text{--}40^\circ$ , it evolves red fumes and is converted into the nitrosohydrazone referred to above. A small amount of benzylamine is also produced in the reduction of benzaldazine.

Benzylbenzylidenehydrazine is hydrolysed by hydrochloric acid to benzaldehyde and *benzylhydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}_2$ ; the *hydrochloride* of the latter crystallises from alcohol in glistening flakes, dissolves very readily in water, and melts at  $111^\circ$ ; the *base* is a colourless oil, which boils at  $135^\circ$  under 29 mm. pressure, readily decomposes with loss of nitrogen, and condenses like phenylhydrazine with aldehydes, ketones, and ethyl acetoacetate.

*Benzyl-o-hydroxybenzylidenehydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , crystallises from dilute alcohol in pale yellow flakes and melts at  $90^\circ$ .

*Pyruvic acid benzylhydrazone*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{CO}_2\text{H}$ , crystallises from dilute alcohol in stout, white prisms and melts at  $104^\circ$ .

*Benzylsemicarbazide*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises from dilute alcohol and melts at about  $135^\circ$ . *Phenylbenzylthiosemicarbazide*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ , crystallises from alcohol in flakes and melts at  $116^\circ$ . *Dibenzoylbenzylhydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{N}_2\text{HBz}_2$ , crystallises from dilute alcohol in prisms and melts at  $148^\circ$ . Hydrochloric acid slowly hydrolyses benzylhydrazine to benzyl chloride and hydrazine.

By reduction with zinc dust and acetic acid, benzaldazine is converted into ammonia and dibenzylamine. *p*-Methylbenzaldazine is similarly reduced to *di-p-methylbenzylamine*,  $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$ ; the *hydrochloride* crystallises from alcohol in glistening flakes and melts at  $272^\circ$ ; the *base* forms stout, tabular crystals, melts at  $32.5^\circ$ , and boils at  $192\text{--}193^\circ$  under 13 mm. pressure; the *nitrate* forms white tablets, only slightly soluble in water, and melts at  $213^\circ$ ; the *picrate* crystallises from alcohol or light petroleum in stout, red tablets and melts at  $153^\circ$ ; the *platinichloride* forms pale yellow flakes and melts at  $188^\circ$ ; the *mercurichloride* separates from dilute alcohol in large crystals and melts at  $112^\circ$ ; the *nitrite* melts at  $145^\circ$  and can be crystallised from alcohol; it is, however, readily converted into the *nitroso*-derivative, which separates from alcohol in colourless needles and melts at  $52^\circ$ .

When reduced with sodium amalgam, *p*-methylbenzaldazine is converted into *p-methylbenzyl-p-methylbenzylidenehydrazine*,



which crystallises from alcohol in large tablets, melts at  $101^{\circ}$ , does not reduce Fehling's solution, and rapidly decomposes in the air; the *picrate* crystallises from alcohol in golden-yellow needles and melts at  $132^{\circ}$ ; the *acetyl* derivative crystallises from alcohol in thick flakes and melts at  $95^{\circ}$ ; the *benzoyl* derivative crystallises from alcohol in minute needles and melts at  $130.5^{\circ}$ ; the *nitroso*-derivative crystallises from alcohol in yellow needles, melts at  $111^{\circ}$ , gives Liebermann's reaction, and is decomposed by dilute hydrochloric acid with formation of *p*-tolylaldehyde. *Di-p-methylbenzyl-di-p-methylbenzylidenehydrotetrazone*,  $N_2(CH_2 \cdot C_6H_4Me)_2(N \cdot CH \cdot C_6H_4Me)_2$ , prepared by oxidising the hydrazone with mercuric oxide, crystallises from alcohol in minute needles and melts at  $163^{\circ}$ ; excess of the oxide gives *p*-methylbenzaldazine; hydrochloric acid gives *p*-methylbenzaldazine and *p*-tolaldehyde.

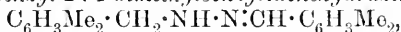
The hydrazone is further reduced by sodium amalgam to *s-di-p-methylbenzylhydrazine*,  $N_2H_2(CH_2 \cdot C_6H_4Me)_2$ ; the *hydrochloride* is insoluble in cold water, crystallises from dilute alcohol in minute, glistening needles, and melts at  $236^{\circ}$ ; the *base* separates from ether in pale yellow crystals, melts at  $67^{\circ}$ , and rapidly decomposes; the *diacetyl* derivative crystallises from alcohol in minute, colourless needles and melts at  $112^{\circ}$ ; nitrous acid converts the hydrazine into the nitroso-derivative of the hydrazone; picric acid also yields the *picrate* of the hydrazone; mercuric oxide oxidises it directly to methylbenzaldazine.

*p-Methylbenzylhydrazine hydrochloride*,  $C_6H_4Me \cdot CH_2 \cdot NH \cdot NH_2 \cdot HCl$ , prepared by hydrolysing the hydrazone with hydrochloric acid, crystallises from alcohol in glistening plates and melts at  $152^{\circ}$ ; the *base* boils at  $135^{\circ}$  under 18 mm. pressure, solidifies to a crystalline mass which melts at  $40-41^{\circ}$ , and reduces Fehling's solution and ammoniacal silver solutions in the cold; the *picrate* crystallises from water in yellow needles and melts with decomposition at  $144^{\circ}$ . *p-Methylbenzyl-o-hydroxybenzylidenehydrazine*,  $OH \cdot C_6H_4 \cdot CH : N \cdot NH \cdot CH_2 \cdot C_6H_4Me$ , crystallises from alcohol in pale yellow, glistening flakes and melts at  $105^{\circ}$ . *p-Methoxybenzyl-p-methylbenzylidenehydrazine* crystallises from dilute alcohol in microscopic needles and melts at  $88^{\circ}$ . *Pyruvic acid p-methylbenzylhydrazone*,  $CO_2H \cdot CMe : N_2H \cdot CH_2 \cdot C_6H_4Me$ , crystallises from alcohol in glistening plates and melts at  $77-78^{\circ}$ . *p-Methylbenzylsemicarbazide*,  $C_6H_4Me \cdot CH_2 \cdot NH \cdot NH \cdot CO \cdot NH_2$ , crystallises from dilute alcohol in white flakes and melts at about  $142^{\circ}$ . *p-Methylbenzyl-phenylthiosemicarbazide* crystallises from dilute alcohol in large, glistening flakes and melts at  $132-133$ . *1-p-Methylbenzyl-3-methyl-5-pyrazolone*,  $C_6H_4Me \cdot CH_2 \cdot N < \begin{smallmatrix} N=CMe \\ CO \cdot CH_2 \end{smallmatrix}$ , melts at  $154-155^{\circ}$ . *Di-benzoyl-p-methylbenzylhydrazine*,  $C_6H_4Me \cdot CH_2 \cdot N_2HBz_2$ , crystallises from alcohol in needles and melts at  $165^{\circ}$ . *p-Methylbenzylhydrazine* is hydrolysed by hydrochloric acid to hydrazine hydrochloride and *p*-methylbenzyl chloride, and the latter was characterised by converting it by Gabriel's method (Abstr., 1887, 1037) into *p-methylbenzyl-phthalimide*, which crystallises from dilute alcohol in long, white needles and melts at  $116-117^{\circ}$ .

*2:4-Dimethylbenzaldazine*,  $N_2(CH \cdot C_6H_3Me_2)_2$ , separates from alcohol in stout crystals and melts at  $118^{\circ}$ ; the *hydrochloride* crystallises from

alcohol in small, glistening, yellow needles and melts at 178—179° with evolution of gas. It is reduced by zinc dust and acetic acid to 2:4-dimethylbenzylamine (Hinrichsen, Abstr., 1889, 131) and *di*-2:4-dimethylbenzylamine,  $\text{NH}(\text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2)_2$ , which boils at 217—218° under 14 mm. pressure, and solidifies at 28.5°; the *hydrochloride* crystallises from water in colourless needles and melts at 226—227°; the *nitrate* forms large, white tablets, melts with decomposition at 211°, and is only very slightly soluble in hot water; the *picrate* crystallises from alcohol in indistinct, sulphur-yellow crystals and melts at 142—143°; the *platinichloride* separates from alcohol in red-brown crystals and melts with decomposition at 188°; the *mercurichloride* separates from alcohol in well-formed crystals and melts at 157°; the *nitrite* crystallises from alcohol in small, colourless needles, melts at 147°, and is converted, by evaporating with alcohol, into *nitrosodi*-2:4-dimethylbenzylamine, which separates from alcohol in small, pale yellow crystals and melts at 73°.

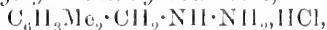
2:4-Dimethylbenzyl-2:4-dimethylbenzylidenehydrazine,



prepared by reducing the aldazine with sodium amalgam, crystallises from alcohol in glistening needles, melts at 77—78°, and decomposes rapidly; the *picrate* crystallises from alcohol in bunches of yellow needles and melts at 127—128°; the *acetyl* derivative crystallises from alcohol in long, hair-like needles and melts at 137.5°; the *benzoyl* derivative crystallises from alcohol in felted needles and melts at 136°; the *nitroso*-derivative crystallises from alcohol in bundles of long, yellow needles and melts at 68°. *Di*-2:4-dimethylbenzyl-*di*-2:4-dimethylbenzylidenehydrotetrazone,  $\text{N}_2(\text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2)_2(\text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_3\text{Me}_2)_2$ , separates from alcohol in pale yellowish granules and melts at 137—138° with evolution of gas.

*s*-*Di* 2:4-dimethylbenzylhydrazine,  $\text{N}_2\text{H}_2(\text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2)_2$ , prepared by further reduction of the hydrazone with sodium amalgam, crystallises from alcohol in long, white needles, melts at 58.5°, and gradually decomposes in the air; the *hydrochloride* crystallises from alcohol in glistening, white needles, melts at 200°, and is almost insoluble in boiling water; the *diacetyl* derivative crystallises from alcohol in colourless flakes and melts at 125°; nitrous acid converts the hydrazine into the nitroso-derivative of the hydrazone; mercuric oxide oxidises it to the tetrazone and the aldazine.

2:4-Dimethylbenzylhydrazine hydrochloride,



crystallises from alcohol in long, glistening needles, melts at 170—171°, and reduces ammoniacal silver and Fehling's solutions in the cold. 2:4-Dimethylbenzylbenzylidenehydrazine,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$ , crystallises from alcohol in short, stout needles, melts at 92—93°, and is fairly stable in the air.

2:4:5-Trimethylbenzyl-2:4:5-trimethylbenzylidenehydrazine,



crystallises from alcohol in unstable, silky needles and melts at 131°; the *picrate* crystallises from ether in yellow needles and melts at 169°; the *acetyl* derivative crystallises from alcohol in long, slender needles and melts at 181°; the *benzoyl* derivative crystallises from alcohol in

long needles and melts at  $187^{\circ}$ ; and the *nitroso*-derivative melts at  $118^{\circ}$ .

*s-Di-2:4:5-trimethylbenzylhydrazine*,  $N_2H_2(CH_2 \cdot C_6H_2Me_3)_2$ , crystallises from alcohol in unstable, rhombic crystals and melts at  $128^{\circ}$ ; the *hydrochloride* crystallises from alcohol in long, hair-like needles, melts at  $170-171^{\circ}$ , and is only slightly soluble in water; nitrous and picric acids yield derivatives of the hydrazone.

*2:4:5-Trimethylbenzylhydrazine*,  $C_6H_2Me_3 \cdot CH_2 \cdot NH \cdot NH_2$ , solidifies to a mass of white crystals and rapidly decomposes with loss of nitrogen; the *hydrochloride* crystallises from water or alcohol in needles and melts at  $239-240^{\circ}$ ; the *picrate* crystallises from alcohol in yellow, monoclinic needles and begins to decompose at  $163^{\circ}$ . *2:4:5-Trimethylbenzylbenzylidenhydrazine*,  $C_6H_2Me_3 \cdot CH_2 \cdot NH \cdot N : CHPh$ , crystallises from alcohol in unstable tablets and melts at  $89-90^{\circ}$ . *2:4:5-Trimethylbenzylsemicarbazide*,  $C_6H_2Me_3 \cdot CH_2 \cdot NH \cdot NH \cdot CO \cdot NH_2$ , crystallises from water in white needles and melts at  $174-175^{\circ}$ . *Phenyl-2:4:5-trimethylbenzylthiosemicarbazide*,  $C_6H_2Me_3 \cdot CH_2 \cdot NH \cdot NH \cdot CS \cdot NHPh$ , crystallises from alcohol in silky needles and melts at  $167-168^{\circ}$ . *Pyruvic acid 2:4:5-trimethylbenzylhydrazone*,  $C_6H_2Me_3 \cdot CH_2 \cdot NH \cdot N : CMe \cdot CO_2H$ , crystallises from alcohol in silky needles and melts at  $91-92^{\circ}$ . T. M. L.

**Combination of Magenta with the Sulpho-conjugated Azo-colouring Matters.** By ALPHONSE SEYEWETZ (*Compt. rend.*, 1900, 131, 472-474).—Naphthylamine-brown, crystallised ponceau, and solid red D, which contain respectively 1, 2, and 3 sulphonic groups neutralised by an alkali, combine respectively with 1, 2, and 3 mols. of magenta. In presence of an excess of alkali, however, naphthylamine-brown will combine with 2 mols. of magenta; it is the only one of the three that contains a hydroxyl group in a nucleus in which the sulphonic group has not been substituted.

Tropæolin V, chrysoin, Orange I and Orange II, which contain one sulphonic group and various hydroxyl groups, each combine with 1 mol. of magenta when the sulphonic group only is neutralised, but in presence of excess of alkali, they each combine with 2 mols. of magenta. In all of them there is at least one hydroxyl group in a nucleus in which the sulphonic group has not been introduced.

Crystallised ponceau, chromotrope 2R, chrome-brown RR, solid yellow A, jaune soleil, brilliant crocein M, Congo-red, and diamine-black BO all contain two sulphonic groups, together with various substituted radicles, and all combine with 2 mols. of magenta, but chrome-brown RR, which is the only one containing a hydroxyl group in a nucleus that does not contain a sulphonic group, combines with 3 mols. of magenta in presence of sufficient alkali to neutralise the hydroxyl group.

Ponceau 5R and diamine-blue combine with as many mols. of magenta as they contain sulphonic groups neutralised by an alkali, but benzo-orange R combines with 2 mols. magenta, probably owing to the presence of a carboxyl group. It contains a hydroxyl group in a nucleus which does not also contain a sulphonic group, and consequently in presence of excess of alkali it combines with a third mol. of magenta. C. H. B.

**Isomeric Forms of Diazoaminobenzenedi-*p*-sulphonic Acid.** By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1900, 31, 762—763).—Whereas the diazoamino-compound prepared from sodium sulph-anilate at 0° is sparingly soluble in water and crystallises in slender, yellow needles, that obtained at 10—14° is easily soluble and is only precipitated by saturating the solution with common salt and adding a large quantity of glacial acetic acid. The yellowish-brown powder thus obtained is contaminated with sodium chloride and sodium acetate, but a determination of the ratio of sulphur to nitrogen shows it to have the same composition as the product obtained at 0°. Moreover, the latter on heating at 100° yields the corresponding amino-azo-compound, yet the soluble modification remains unchanged. It is suggested that the sparingly soluble modification probably has the formula  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , and the soluble modification either the formula  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N} > \text{NH}$  or  $\text{NH}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2$ .

W. A. D.

**Influence of Nitrogenous Substances on the Heat-coagulation of Proteids.** By KARL SPIRO (*Zeit. physiol. Chem.*, 1900, 30, 182—199).—The observations were made on various proteids, but mostly on egg-albumin. Increase in the concentration of the solution lowers the coagulating point somewhat. It is necessary to take this factor and also the rate of heating into account. Choline, as Mauthner (*Med. Jahrbücher*, 1874, 347) originally stated, lowers the coagulation point, and ultimately prevents coagulation; and its solutions will even dissolve fibrin and coagulated albumin. Other basic substances, such as piperidine, pyridine, aniline, and xylydine, act similarly. Beyond a certain point, pyridine and urethane precipitate proteid in the cold. Formamide in small quantities raises the coagulating point; increase in its amount depresses it; finally, there is precipitation in the cold, but on heating, the proteid remains in solution. Urea in small amount raises the coagulation point considerably, but with greater concentration prevents coagulation entirely. Considerable importance is attached to these experiments with urea, on account of the occurrence of proteids in urine. The action of urea resembles that of alkalis, and a substance analogous to alkali-albumin is believed to be formed.

W. D. H.

**Bence-Jones Albumin.** By ADOLF MAGNUS LEVY (*Zeit. physiol. Chem.*, 1900, 30, 200—210).—A case of Bence Jones albumin occurring in the urine is described, and the characters of this remarkable proteid are examined in full. The case was one of bone disease, apparently similar to those in which the condition has been previously described. A review of the previous cases described leads to the conclusion that the same proteid occurred in all. The most noteworthy difference of opinion here expressed between the present author and those who preceded him is that the proteid is not an albumose, but an albumin, on the ground of elementary analysis and its reactions. Under certain conditions, it is completely coagulated by heat; here Spiro's observations (see preceding abstract) are duly taken into account. On digestion with gastric juice, it yields the usual series of

digestive products, with the exception of hetero-albumose. By slow concentration of a solution in ammonium sulphate, the proteid was obtained in a crystalline form.

It is believed to originate, not from the small bony tumours, but from the liver. The same opinion was expressed by Noël Paton respecting his crystalline globulin. How the bone disease affects the metabolism in the liver so as to lead to the discharge of this proteid remains an open question.

W. D. H.

**Proteids of the Egg Yolk.** By THOMAS BURR OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, 22, 413—422).—Sodium chloride solutions dissolve from egg yolk a large amount of substance which is precipitated on diluting or dialysing the solution. This globulin contains 15—30 per cent. of lecithin, and of the fractions that are obtained by fractional precipitation, those which are the more soluble contain the more lecithin; these compounds might well be called *lecithin-nucleovitellin*. The lecithin is removed readily by alcohol, but not by ether.

The insoluble proteid free from lecithin, *nucleovitellin*, has a constant composition when prepared from different fractions of the lecithin compound; when digested with pepsin, it yields paranuclein of varying composition. If all the phosphorus in these two substances is assumed to be present as  $H_3PO_4$  or  $H_5P_3O_9$  (or some very simple organo-phosphoric acid), and the amounts of hydrogen, oxygen, and phosphorus in this are subtracted from those found in the original substances, the composition of the remainder is the same whether the substance under consideration is the paranuclein or the paranucleo-proteid from which it is derived. Probably, therefore, both substances are compounds, in different proportions, of the same proteid, *vitellin*, with some derivative of phosphoric acid. The composition of the two substances named is:

	C.	H.	O (diff.).	N.	S.	P.
Nucleovitellin...	51.24	7.16	23.21	16.38	1.04	0.94
Vitellin .....	52.71	7.46	22.14	16.64	1.05	—

C. F. B.

**Influence of Phosphates and other Inorganic Compounds on the Proteolytic Diastase of Malt.** By AUG. FERNBACH and L. HUBERT (*Compt. rend.*, 1900, 131, 293—295. Compare this vol., i, 576).—The activity of the proteolytic diastase of malt is greatly increased by the addition of acid just up to the point at which the alkalinity to methyl-orange is neutralised, but if this limit is exceeded in the smallest degree the activity of the diastase is markedly reduced. Alkali phosphates have a retarding effect due to their alkalinity. Salts of calcium, magnesium, and aluminium, which precipitate part of the phosphates, accelerate the action of the diastase, but when added in excess may exert a distinctly retarding action. The different results obtained with diastases partially purified by precipitation with alcohol, &c., are probably due to the more or less complete removal of some of the phosphates.

C. H. B.

## Organic Chemistry.

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**Composition of Roumanian Petroleum.** By PETRU PONI (*Chem. Centr.*, 1900, ii, 452; from *Anal. Acad. romane*, 23).—The composition of petroleum from Colibasi has been determined by fractionally distilling from 0—100°. The petroleum does not contain acetylene or ethylene hydrocarbons, but in the fraction boiling below 10° small quantities of ethane, propane, butane, *n*-pentane, and *tert*.pentane were found. From the portion boiling at 26—36°, *isopentane* was isolated; this, when oxidised by fuming nitric acid, forms carbon dioxide, acetic acid, and two solid substances which have not yet been examined. The fraction distilling at 50—52° has a maximum sp. gr. 0.6963 at 0°/0°, and, therefore, probably contains *cyclopentane* and *tert*.hexane. Several isomeric hexanes also appeared to be present in the fraction boiling at 58—70°. The portion boiling at 64—66° to 74—76° contained small quantities of benzene which passed over with the hexane and *methylcyclopentane* vapours. *Methylcyclopentane* boils at 70—72°, and, on oxidation by fuming nitric acid, not only yields carbon dioxide and acetic acid, but also oxalic, succinic, and glutaric acids. The fraction boiling at 80—82° has a sp. gr. 0.7664 at 0°/0°, and contained *cyclohexane*, whilst that at 90—100° consisted largely of heptane mixed with toluene. The fraction obtained at 90—92° showed a minimum sp. gr. These fractions probably also contained *methylcyclohexane* which boils at 102°, for after removing toluene and rectifying eight times, the sp. gr. was still 0.7345—0.7515. E. W. W.

**Decomposition of Viscous Substances (Lubricating Oils) by Distillation under Pressure.** By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1900, 33, 2265—2270).—When phenylxylylethane, boiling at 270—310°, obtained from crude xylene by treatment with sulphuric acid, is distilled under a pressure of 10 atmospheres, methylanthracene, anthracene, toluene, and  $\psi$ -cumene are produced, together with a gas consisting chiefly of hydrogen and methane. Dicumyldimethylmethane behaves similarly when distilled under pressure, yielding dimethylanthracene, tetramethylbenzene, xylene, and toluene.

When resin oil, 90 per cent. of which boils at 330—355° and has the composition  $C_{18}H_{28}$ , is distilled under a pressure of 25 atmospheres, phenanthrene, methylphenanthrene, cymene, methyleymene, and hydrocarbons richer in hydrogen are obtained, together with methane, hydrogen, and small quantities of olefines.

If 'bakunin' (lubricating oil prepared from Baku naphtha), boiling at 360—420°, is distilled under 25 atmospheres pressure, the products consist of naphthalene, paraffins, a considerable quantity of olefines, and a gas composed of methane and unsaturated hydrocarbons.

The authors conclude that the lubricating oils are not composed of polymeric olefines, but consist of cyclic compounds formed by the condensation of two or more molecules of hydrocarbons of the olefine or acetylene series. E. G.

**Products of the Explosion of Acetylene and of Mixtures of Acetylene and Nitrogen.** By WILLIAM G. MIXTER (*Amer. J. Sci.*, 1900, [iv], 10, 299—309. Compare this vol., i, 197).—The amounts of acetylene and hydrogen cyanide left after exploding mixtures of acetylene and nitrogen have been determined under a large variety of conditions. As a rule these amounts tend to increase as the proportion of nitrogen in the mixture increases, but the results are not regular; ammonia was detected in some cases, but not cyanogen. No hydrogen cyanide was formed when the gas was exploded in an iron U-tube cooled with water, but mixtures of acetylene and ammonia gave hydrogen cyanide when the gas was merely fired in an open jar at a comparatively low temperature. The relationship between the initial pressure and the amount of acetylene found after explosion has not been fully determined, but the quantity of acetylene increases up to 4 per cent. at 3 atmospheres pressure, and diminishes again at 5 atmospheres; the rapid cooling on exploding the gas in an iron U-tube causes no increase in the amount of acetylene, thus confirming the view that the acetylene found after the explosion is not an undecomposed residue, but is produced by a partial recombination of carbon and hydrogen. T. M. L.

**History of the Isonitro-compounds.** By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2542—2543).—A controversial paper and claim for priority. W. A. D.

**Compounds of Ethylene and Allyl Alcohol with Mercuric Salts.** By KARL A. HOFMANN and JULIUS SAND (*Ber.*, 1900, 33, 2692—2700).—The authors have confirmed experimentally all the facts dealt with in their former papers (this vol., i, 384 and 386) which have been called into question by Biilmann (this vol., i, 431). Ethyl ether mercury bromide, which Biilmann failed to obtain, dissolves in 6595 parts of absolute alcohol at 24°. Whereas ethanol mercury salts in alkaline solution yield no precipitate with potassium iodide, and a white precipitate, soluble in hot alkalis, with potassium sulphide, the ethyl ether mercury salts give rise in the first case to a white precipitate which changes to the iodide  $(C_2H_5IHg)_n$  on heating, and in the second, to a white precipitate insoluble in hot alkalis. Moreover, the halogen-free, alkaline solution of an ether salt, unlike that of an ethanol salt, gives an insoluble carbonate when saturated with carbon dioxide. Biilmann's supposed ethanol mercuric sulphate is shown to have the composition  $C_6H_{10}O_{12}S_2Hg_4$ . Details are given for preparing the allene compounds of which Biilmann doubted the existence; since allenemercury nitrate,  $C_3H_3 \cdot HgNO_3$ , is much more stable towards acids and oxidising agents (potassium permanganate and iodine) than allyl oxide mercuric nitrate, it appears probable that it is a mesitylene derivative,  $(C_3H_3 \cdot HgNO_3)_3$ , formed by polymerisation.

Under special conditions allyl alcohol interacts with mercuric salts in alkaline solution to yield *propylene glycol mercuric salts* of the type  $C_3H_7O_2 \cdot HgX$ , which differ strikingly from the allene and allyloxide salts previously described. *Propylene glycol mercuric bromide*,  $C_3H_7O_2 \cdot HgBr$ , melts at 84—86°, decomposes at 110°, is easily soluble in alcohol and acetone, and is rapidly decomposed by hydrochloric acid; the alkaline



solution gives no precipitate with potassium iodide or cyanide or with hydrogen sulphide. Propenolmercuric bromide, on the other hand, melts at  $251^{\circ}$ , is insoluble in organic solvents, and is not attacked by dilute hydrochloric acid; with potassium iodide or cyanide or with hydrogen sulphide, the alkaline solution yields a white, insoluble iodide, cyanide, or sulphide. The glycol iodide,  $C_3H_7O_2 \cdot HgI$ , melts at about  $80^{\circ}$ , and closely resembles the bromide; it is decomposed by acetic acid with separation of mercuric iodide. Propenolmercuric iodide melts at  $271^{\circ}$ , and is not changed by 20 per cent. hydrochloric acid at the ordinary temperature.

W. A. D.

**Some New Derivatives belonging to the Sugar Group.** By WILLIAM ALBERDA VAN EKENSTEIN and CORNELIS A. LOBBY DE BRUYN (*Rec. Trav. Chim.*, 1900, 19, 178—182).—*Tribenzylidene-d-sorbitol*, obtained by the condensation of sorbitol with benzaldehyde in presence of hydrochloric acid, melts at  $185^{\circ}$  and has a rotatory power  $[\alpha]_D + 30^{\circ}$  in 0.4 per cent. chloroform solution. *d*-Mannitol condenses with *o*-, *m*-, and *p*-nitrobenzaldehyde to form crystalline compounds which melt at  $214^{\circ}$ ,  $247^{\circ}$ , and  $162^{\circ}$  respectively and have rotatory powers  $[\alpha]_D - 59^{\circ}$ ,  $-30^{\circ}$ , and  $-16^{\circ}$  in 0.4 per cent. chloroform solution. *d*-Sorbitol reacts with *p*-nitrobenzaldehyde to form a compound which melts at  $150^{\circ}$  and has a rotatory power  $[\alpha]_D - 58^{\circ}$ . Experiments with dulcitol yielded negative results. *L*-Gulonic acid yields a monobenzaldehyde derivative which forms crystalline sodium and potassium salts, melts at  $174^{\circ}$ , and has a rotatory power  $[\alpha]_D - 67^{\circ}$  in 1 per cent. methyl alcoholic solution. *L*-Idosaccharic acid reacts with 2 mols. of benzaldehyde to form a compound which melts at  $211^{\circ}$  and has a rotatory power  $[\alpha]_D - 27^{\circ}$  in 0.4 per cent. methyl alcoholic solution; the sodium and potassium salts are syrupy. In the compounds formed by the condensation of *d*- and *L*-iditol with formaldehyde, three mols. of the latter are concerned, and not two as formerly stated. *L*-Trihydroxyglutaric acid (xylotrihydroxyglutaric acid) reacts with 1 mol. of formaldehyde to form a well crystallised compound which melts at  $242^{\circ}$  and is inactive. *L*-Gulonic acid reacts with two mols. of formaldehyde to form a compound which melts at  $177^{\circ}$  and has a rotatory power  $[\alpha]_D - 88^{\circ}$  in 1 per cent. alcoholic solution. *L*-Idonic acid yields a similar compound which melts at  $226^{\circ}$  and has a rotatory power  $[\alpha]_D - 54^{\circ}$  in 0.4 per cent. methyl alcoholic solution. *L*-Glucose forms a crystalline, yellowish *phenylbenzylhydrazone* which melts at  $124^{\circ}$  and has a rotatory power  $[\alpha]_D - 21^{\circ}$  in 0.5 per cent. methyl alcoholic solution.

N. L.

**Dimethyl Sulphate as an Alkylating Agent.** By FURTZ ULLMANN and P. WENNER (*Ber.*, 1900, 33, 2476—2477).—Dimethyl sulphate can replace methyl iodide in all cases, and in general acts more rapidly and better; as it boils at  $188^{\circ}$ , open vessels may be used and the necessity for sealed tubes obviated. Aniline (2 mols.) with dimethyl sulphate (1 mol.) forms methylaniline and aniline methyl sulphate; *m*-nitraniline is converted into *m*-nitrodimethylaniline. Phenols can be methylated in a manner similar to the Schotten-Baumann method of benzoylation. The sodium salts of aromatic sulphonic acids are converted into methyl salts. Quinolines are con-

verted into quinolinium compounds, "aminonaphthacridines," phenyl-acridines, diaminoacridines, &c., into acridinium compounds, and aminophenazines into phenazonium compounds. Only the ring nitrogen is methylated in the latter cases; the amino-groups are not attacked, probably because the insoluble methyl-sulphate is precipitated before there has been time for a further action of the dimethyl sulphate to take place. C. F. B.

**Decomposition of Alkyl Nitrates and Nitroglycerol by Alkalis, and the Relative Stability of Explosives.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 519—521).—When potassium hydroxide acts on nitroglycerol even in dilute solution, some potassium nitrite is formed, and hence it would seem that either some glyceraldehyde is produced during the reaction, which would then be analogous to the action of the alkali on ethyl nitrate, or the formation of aldehyde, and partial reduction of the nitric acid take place during the first action of the latter on the glycerol. In the latter case, the product, instead of being pure nitroglycerol, will be a nitroso-nitro-compound, and the presence of the nitrous acid derivative may exert an important influence on the stability of the compound. The presence of the nitroso-compound would not be detected by the ordinary method of analysis. C. H. B.

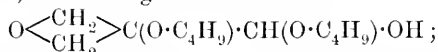
**Reaction of Nitrous Esters with Alcohols and Ketones in Presence of Excess of Hydrogen Chloride [in Alcoholic Solutions].** By J. KISSEL (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 390—419).—By the action of hydrogen chloride and ethyl alcohol on *isoamyl* nitrite, an ether of the composition  $C_{15}H_{30}O_3$  is obtained (*J. Russ. Phys. Chem. Soc.*, 1896, 28, 882), and on heating with hydriodic acid in sealed tubes, this yields *isoamyl* iodide and a small proportion of ethyl iodide; the presence of the latter shows that the ethyl alcohol takes part in the formation of the ether.

When *isoamyl* nitrite, *isoamyl* alcohol, and hydrogen chloride react together, a colourless, oily compound,  $C_{10}H_{22}O_2$ , is obtained, which is volatile in a current of steam, boils at  $170-173^\circ$ , and is probably the *isoamyl* ether of ethylene glycol; it could not be obtained quite free from chlorine. On oxidation with alkaline permanganate, it yields (1) *α-ethoxy-γ-amyl oxyisovaleric acid*,  $C_5H_{11} \cdot O \cdot CMe_2 \cdot CH(OEt) \cdot CO_2H$ , a faint yellow, viscous liquid, slightly soluble in water, but readily so in aqueous ammonia or caustic alkalis, of which the *silver* and *calcium* salts were prepared; (2) oxalic acid, and (3) another acid, not yet identified, the silver salt of which forms pale yellow, granular crystals, and contains 38.41 per cent. of metal. If the oxidation is carried further, the last-named acid is found among the products, together with *isovaleric* acid and an ether-like substance boiling at  $123-125^\circ$  under 40 mm. pressure.

In the reaction yielding the ether,  $C_{15}H_{30}O_3$ , various nitrogenous compounds are formed which are soluble in sodium hydroxide solution, and on adding a solution of a copper or mercury salt to the alkaline liquid a precipitate is at first formed, but afterwards dissolves; the action of hydrogen sulphide precipitates the metal, and yields a

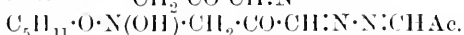
compound,  $C_{10}H_{19}O_3N$ , to which is ascribed the constitution  $O-CH \cdot C_2H_4 \cdot O \cdot CH_2$   
 $\begin{array}{c} | \quad >CH_2 \quad | \\ CH_2 \cdot N \cdot O \cdot C_2H_4 \cdot CHMe \end{array}$ ; it is a thick, brown syrup, which has a faint narcotic smell, is almost insoluble in water, and is not acted on by acids or alkalis, whilst with concentrated hydriodic acid it yields a basic compound.

The action of alcoholic hydrochloric acid on *isobutyl nitrite* in presence of alcohol gives rise to four compounds: (1) a *liquid* boiling at  $175-178^\circ$  under 18 mm. pressure, and having the constitution  $C_4H_9 \cdot O \cdot CMe_2 \cdot CH(OEt) \cdot OH$ ; (2) a *liquid* boiling at  $180-188^\circ$  under 18 mm. pressure, and having the constitution



(3) *oxalic acid*, and (4) a brown, syrupy *acid* yielding a *calcium salt*, which, on analysis, gives results agreeing with those required for the formula  $(C_4H_9 \cdot O \cdot CMe_2 \cdot CO_2)_2Ca$ . Oxidation of compound (1) by means of an alkaline solution of potassium permanganate gives an *acid*, the silver salt of which has the composition  $C_{10}H_{19}O_4Ag$  or  $C_{10}H_{19}O_5Ag$ .

The action of alcoholic hydrogen chloride on a mixture of acetone and *isoamyl nitrite* in molecular proportion yields (1) *isoamyloxyacetone*,  $COMe \cdot CH_2 \cdot O \cdot C_5H_{11}$ , which is a colourless liquid with a pleasant smell, and boils at  $140-142^\circ$  under 25 mm. pressure. With phenylhydrazine, it gives the *compound*  $N_2HPh(CMe \cdot CH \cdot NH \cdot NHPh)_2$ , which separates from alcohol in pale yellow plates, darkens in the air, and melts at  $147^\circ$ ; on adding a little of this substance to concentrated sulphuric acid, a dirty-green coloration is formed, changing to yellow; (2) *s-diisoamyloxyacetone*,  $CO(CH_2 \cdot OC_5H_{11})_2$ ; (3) a hard, brown, hygroscopic *resin*, having a faint narcotic smell and the probable constitution  $C_5H_{11} \cdot O \cdot N \begin{array}{c} \diagup CH_2 \cdot CO \cdot CH \cdot N \\ \diagdown CH_2 \cdot CO \cdot CH \cdot N \end{array} > O$ , or



It gives a *mercury salt*,  $C_{11}H_{19}O_4N_3 \cdot HgCl_2 \cdot 2HgCl$ , and with nitrous acid yields the *compound*.



The products of the interaction of methyl propyl ketone, *isoamyl nitrite*, and hydrochloric acid in alcoholic solution are (1) the *compound*,  $OH \cdot CH_2 \cdot CO \cdot [CH_2]_2 \cdot CH \cdot N \cdot O \cdot C_5H_{11}$ , boiling at  $165-170^\circ$  under 15 mm. pressure; (2) a *compound*,  $C_{15}H_{25}ON_3$ , which boils at  $204-214^\circ$ , under 25 mm. pressure, and gives with mercuric chloride a white, amorphous precipitate of the composition  $C_{15}H_{25}ON_3 \cdot HgCl_2 \cdot HgCl$ ; (3) an amorphous, brown, hygroscopic *compound*,  $C_{20}H_{33}O_9N_5$ , which has a slightly narcotic odour, and forms a *mercury derivative*,  $C_{20}H_{33}O_9N_5 \cdot HgCl_2 \cdot 2HgCl$ . T. H. P.

**Preparation of Lecithin.** By PETER BERGELL (*Ber.*, 1900, 33, 2584-2586).—Lecithin is best prepared by extracting egg yolk with 96 per cent. alcohol and precipitating with cadmium chloride at  $0^\circ$ ; the precipitate is then extracted with ether, and decomposed by boiling with alcohol and ammonium carbonate. The lecithin separates from the alcoholic solution at  $-10^\circ$ , and may be purified by being

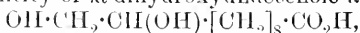
dissolved in chloroform and precipitated with acetone. A further quantity may be obtained from the alcoholic mother liquor. The yield is about 4 per cent. of the yolk. The sample obtained yielded palmitic, stearic, and oleic acids, and an attempt to prepare a sample by fractional precipitation which would only yield one acid proved unsuccessful. The platinichloride when quite dry is insoluble in ether, but dissolves readily after having been moistened with water.

Lecithin, contrary to the statement of Diaconoff (*Annalen*, 1868, 148, 77), can be powdered and preserved in an exhausted vessel.

A. H.

**Constituents of Cascarilla Oil and Undecenoic Acid.** By HERMANN THOMS (*Chem. Centr.*, 1900, ii, 574—575; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1899, ii, 648—652).—In cascarilla oil, G. Fendler has found 2.10 per cent. of free acid, 0.30 of eugenol, 10 of a terpene,  $C_{10}H_{16}$ , boiling at 155—157°, 8.8 of *l*-limonene, 13.2 of *p*-cymene, 10.5 of a sesquiterpene,  $C_{15}H_{24}$ , boiling at 255—257°, 33 of a sesquiterpene boiling at 260—265°, 11 of an alcohol,  $C_{15}H_{23}\cdot OH$ , boiling at 280—290°, 10 of compounds of higher boiling point containing oxygen, and 1.1 of resin. The *terpene*, which boils at 155—157°, forms oily additive compounds with  $HCl$  and  $2Br$ , and is not identical with pinene; the *nitrosochloride*,  $C_{10}H_{16}ONCl$ , melts at 91—92°, and the *nitropiperidide*,  $NO\cdot C_{10}H_{16}\cdot C_5NH_{10}$ , at 112°. In addition to palmitic and stearic acids, the oil contains *cascarillie acid*,  $C_{11}H_{20}O_2$ , which distils as an oil; it boils at 268—270°, solidifies at about  $-18^\circ$ , has a sp. gr. 0.9324 at  $20^\circ$ , and is scarcely attacked by potassium permanganate. The *amide*,  $C_{10}H_{19}\cdot CO\cdot NH_2$ , melts at  $78^\circ$ . By the action of fuming nitric acid on cascarillie acid, a small quantity of an unsaturated acid,  $C_{11}H_{18}O_4$ , is formed; it crystallises in lustrous leaflets and melts at  $111^\circ$ .

Undecenoic acid,  $CH_2\cdot CH\cdot [CH_2]_8\cdot CO_2H$ , is oxidised by fuming nitric acid at  $60^\circ$ , forming sebacic acid,  $CO_2H\cdot [CH_2]_8\cdot CO_2H$ , whilst by the action of potassium permanganate at the ordinary temperature it yields a small quantity of *κ*-dihydroxyundecenoic acid,



and at  $0^\circ$  it forms a hydroxyketonic acid,  $OH\cdot CH_2\cdot CO\cdot [CH_2]_8\cdot CO_2H$ . The last-named acid reduces Fehling's solution and ammoniacal silver solutions and also forms a *semicarbazone* which melts at  $145^\circ$ ; by oxidation, or by hydrolysing the hydroxynitrile obtained by means of hydrogen cyanide, sebacic acid is formed.

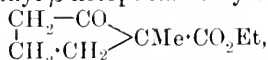
E. W. W.

**Camphoric Acid. IX. Structure and Configuration of *cis-trans*-Campholytic Acid.** By WILLIAM A. NOYES and EDWARD F. PHILLIPS (*Amer. Chem. J.*, 1900, 24, 285—291).—Aminodihydrocampholytic acid (Abstr., 1895, i, 187, 295, 552) in aqueous solution has  $[\alpha]_D +53.7^\circ$ ; 7.6 parts dissolve in 100 parts of water at  $20^\circ$ . The hydroxydihydrocampholytic acid obtained by its decomposition with nitrous acid has a solubility of 2.05 parts in 100 parts of water at  $20^\circ$ , and  $[\alpha]_D +71.85^\circ$ ; the *cis-trans*-campholytic acid formed simultaneously has a sp. gr. 1.0166 at  $13.2^\circ$ , 1.0145 at  $18^\circ$ , and 1.0107 at  $27.5^\circ$ ,  $[\alpha]_D$  being  $-60.4^\circ$ ,  $59.6^\circ$ , and  $58.0^\circ$  at the same temperatures. *β*-Bromodihydrocampholytic acid,  $C_8H_{14}Br\cdot CO_2H$ , obtained

from *cis-trans*-campholytic acid and hydrogen bromide, has  $[\alpha]_D + 90.5^\circ$  in 10 per cent. benzene solution, and is apparently identical with the acid formed from hydroxydihydrocampholytic acid and hydrogen bromide ( $[\alpha]_D + 93.5^\circ$ ).

The bearing of these facts on the question of the configuration of campholytic acid is dealt with at some length. W. A. D.

**Condensations with Ethyl Acetoacetate and their Reversal.** By WILHELM DIECKMANN (*Ber.*, 1900, 33, 2670—2684).—Although ethyl acetoacetate is only slightly changed by boiling with alcoholic sodium ethoxide (1 mol.) for 2 hours, ethyl ethylacetoacetate methylacetoacetate, and benzylacetoacetate are, under similar conditions, completely resolved into acetic acid and the corresponding alkylacetic ester,  $\text{CH}_3\text{R}\cdot\text{CO}_2\text{Et}$  ( $\text{R} = \text{Me, Et, CH}_2\text{Ph}$ ); using a smaller proportion of sodium ethoxide (about 15—20 per cent. of that calculated), the hydrolysis is only very partial after 2 hours, although under the same conditions with dialkylacetoacetic esters ( $\text{CR}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ ,  $\text{R}_2 = \text{Me}_2, \text{Et}_2, \text{Et, CH}_2\text{Ph}$ ) it is complete, acetic acid and a dialkylacetic ester being obtained. These facts are explained by assuming that the ease of decomposition of  $\beta$ -ketonic esters depends on their "acidity," being greatest when this is least. Thus, the "strongly acid"  $\beta$ -ketopentamethylenecarboxylic ester,  $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CO}_2\text{Et}$ , is much more stable towards sodium ethoxide than the closely related "feebly acid" open-chain compound,  $\text{CH}_3\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , whilst the "neutral" ethyl  $\alpha$ -methyl- $\beta$ -ketopentamethylenecarboxylate,



is as easily resolved as the "neutral" dialkylacetoacetic esters,  $\text{CH}_3\cdot\text{CO}\cdot\text{CRet}\cdot\text{CO}_2\text{Et}$ .

The ethyl acetoacetate condensations in presence of sodium ethoxide are thus reversible, in two phases:—

- I.  $\text{ONa}\cdot\text{CMe}(\text{OEt})_2 + \text{CH}_3\cdot\text{CO}_2\text{Et} \rightleftharpoons \text{ONa}\cdot\text{CMe}(\text{OEt})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{EtOH}.$   
 II.  $\text{ONa}\cdot\text{CMe}(\text{OEt})\text{CH}_2\cdot\text{CO}_2\text{Et} \rightleftharpoons \text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} + \text{EtOH}.$

The more "acid" in nature the final  $\beta$ -ketonic ester is, the more stable is its sodium derivative towards alcohol, and hence the less tendency is there to reversal; thus the formation of ethyl acetoacetate from ethyl acetate in presence of sodium ethoxide is much more rapid and complete than that of ethyl dimethylacetoacetate from ethyl acetate and ethyl dimethylacetate, because in the latter case the derivative,  $\text{ONa}\cdot\text{CMe}(\text{OEt})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , initially formed, is very susceptible to decomposition by alcohol. The ease of formation, on the other hand, of, for example, strongly acid diphenylacetoacetic esters from phenylacetoacetic esters (Vollard, *Abstr.*, 1897, i, 422), and of strongly acid, cyclic,  $\beta$ -ketonic-carboxylic esters from adipic and pimelic esters (*Abstr.*, 1894, i, 173) is due to the slight tendency to reversal that exists in these cases.

By the foregoing views, the fact that the decomposition of ethyl dialkylacetoacetates by alcoholic sodium ethoxide is prevented by the presence, in excess compared with the sodium ethoxide

employed, of ethyl acetoacetate or of an ethyl monoalkylacetate, is capable of ready explanation, whilst the need of care to avoid an excess of sodium ethoxide in the Conrad-Limpach method is emphasised. The easy decomposition of dialkylacetoacetic esters by alcoholic sodium ethoxide furnishes, moreover, a means of obtaining dialkylacetic acids which is preferable in many cases to using alkali, because, with the latter, ketonic hydrolysis always occurs.

When ethyl diethylacetoacetate (2 mols.) is heated in absolute ethereal solution for 6 hours with sodium ethoxide (1 mol.) containing only traces of alcohol, ethyl diethylacetate is formed along with *ethyl  $\gamma$ -acetyl- $\beta$ -diethylacetoacetate*,  $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$ , which boils at  $255\text{--}260^\circ$ , and yields a crystalline copper salt melting at  $85^\circ$ ; it is probable that condensation here occurs between the compound  $\text{ONa}\cdot\text{CMe}(\text{OEt})_2$ , formed by the initial decomposition, and unchanged ethyl diethylacetoacetate (compare Conrad and Gast, *Abstr.*, 1898, i, 512).

The following compounds are new: *Ethyl  $\beta$ -phenyl- $\alpha$ -ethylpropionate*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Et}\cdot\text{CO}_2\text{Et}$ , obtained by boiling ethyl ethylbenzylacetoacetate with alcohol containing a small quantity of sodium, boils at  $251\text{--}253^\circ$  (uncorr.). *Ethyl 1-methyl-2-ketohexamethylenecarboxylate*, obtained from ethyl 2-ketohexamethylenecarboxylate and methyl iodide by the Conrad-Limpach method, boils at  $110\text{--}111^\circ$  under 12 mm. pressure, and, with boiling alcoholic sodium ethoxide yields ethyl  $\alpha$ -methylpimelate, which boils at  $140^\circ$  under the same pressure.

W. A. D.

#### New Product of the Destructive Distillation of Tartaric Acid.

By L. J. SIMON (*Compt. rend.*, 1900, **131**, 586—588).—The destructive distillation of tartaric acid in presence of potassium hydrogen sulphate yields about 0.1 per cent. of an acid,  $\text{C}_7\text{H}_8\text{O}_3$ , which is isomeric, but not identical with the pyrotritaric acid (dimethylfurfurancarboxylic acid) of Wislicenus and Stadnicki (*Bull. Soc. Chim.*, 1868, **10**, 489). It softens at about  $158^\circ$ , melts at  $164^\circ$ , and resolidifies at  $156^\circ$ , sublimes readily in white needles or lamellæ, and crystallises from alcohol in prisms, and from water in needles which, after drying at  $100^\circ$ , melt at  $164^\circ$ . It is neutral to helianthin, but acid to phenolphthalein and to litmus; its potassium salt,  $\text{C}_7\text{H}_7\text{O}_3\text{K}\cdot 2\text{H}_2\text{O}$ , is alkaline to all indicators except blue, C4B. The acid and its potassium salt combine readily with bromine and reduce potassium permanganate and silver nitrate in the cold, but do not reduce Fehling's solution.

C. H. B.

*isoPyrotritaric Acid; a New Pyrogenic Product from Tartaric Acid.* By L. J. SIMON (*Compt. rend.*, 1900, **131**, 618—620. Compare this vol., i, 198).—*isoPyrotritaric acid*,  $\text{C}_7\text{H}_8\text{O}_3$ , obtained as a by-product in the dry distillation of tartaric acid, is isomeric with the pyrotritaric acid described by Wislicenus and Stadnicki. It develops a violet coloration with ferric salts closely resembling that obtained from salicylic acid; this colour is changed to orange-red by alkalis; it is not affected by heat, but is removed by concentrated acids and reappears on dilution.

The *ferric* salt,  $\text{Fe}(\text{C}_7\text{H}_7\text{O}_3)_3\cdot 2\text{H}_2\text{O}$ , produced by digesting precipitated ferrichydroxide with a saturated aqueous solution of the acid, forms

deep red crystals giving a red solution. Like ferric salicylate, it may be employed as an indicator in acidimetry. The colour of the solution is not altered by the addition of isopyrotritaric acid, whereas salicylic acid turns it violet; the ferric isopyrotritarate may therefore be used in estimating salicylic acid; it also serves as a reagent for ferric salts, giving a colour reaction in dilutions of 1/100,000. The potassium salt of isopyrotritaric acid gives the same colour reaction as the acid; the oxidation product and the additive compound with bromine obtained from the latter are, however, devoid of this property.

Pyrotartaric acid, the acids of the furfuran series, and pyruvic acid do not give colorations with ferric salts, but the diethyl pyrotartrate obtained from the residues of the distillation of tartaric acid and the last fractions obtained by distilling pyruvic acid under ordinary pressure both exhibit this colour reaction, and contain isopyrotritaric acid.

There is some reason for supposing that the new acid is a hydroxy-dihydrobenzoic acid. G. T. M.

**Pinolic Acid.** By FERDINAND TIEMANN [and MAX KERSCHBAUM] (*Ber.*, 1900, **33**, 2661—2670).—A method is given for the preparation of *i*-pinonic acid in quantity.

*i*-Pinolic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CMe}_2\cdot\text{CHMe} \\ | \\ \text{CH}_2-\text{CH}\cdot\text{OH} \end{smallmatrix}$  is formed when *i*-pinonic acid is heated with alcoholic potash for 6—7 hours at 185—200°; it crystallises in felted needles melting at 99—100°, boils at 195—205° under 20 mm. pressure, is equally sparingly soluble in hot or cold water, dissolves readily in alcohol, ethyl acetate, or ether. On oxidation with potassium permanganate, it affords *i*-pinonic acid.

*l*-Pinolic acid, prepared from *d*-pinonic acid, crystallises in well-formed needles melting at 114—115°. In 33 per cent. alcoholic solution it has a rotation  $-7^\circ$  in a 100 mm. tube.

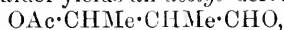
*i*-Pinocampholenic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CMe}_2\cdot\text{CMe} \\ | \\ \text{CH}_2-\text{CH} \end{smallmatrix}$ , is obtained when crude pinolic acid which has not been subjected to treatment with a current of steam is distilled under reduced pressure; the distillate also contains pinodihydrocampholenolactone. It is a transparent, oily liquid having a faint odour, boils at 140—141° under 13 mm. pressure, has a sp. gr. 0.9925 at 17°, and  $n_D$  1.46702, its molecular refraction being 46.97, and the calculated number 47.34. It yields pinodihydrocampholenolactone when treated with hydriodic acid, and when oxidised with permanganate yields the same products as  $\alpha$ -campholenic acid. Active pinocampholenic acid, from *d*-pinonic acid, boils at 136—138° under 10 mm., and at 248—252° under atmospheric pressure. It has a sp. gr. 0.9897 at 20°,  $n_D$  1.47096, and molecular refraction 47.45.

Pinodihydrocampholenolactone, obtained both from pinolic acid and pinocampholenic acid, is a colourless oil with an odour exactly resembling that of dehydrocampholenolactone. It boils at 128—130° under 12 mm., and at 254—257° under atmospheric pressure, has a sp. gr. 1.014 at 18°,  $n_D$  1.4640, and the molecular refraction 45.72, the calculated number being 45.79. When hydrolysed, it yields a hydroxy-acid which does not crystallise, but on distillation yields crystalline pinolic acid.

The foregoing facts are in accordance with Tiemann's formula for pinonic acid, but are scarcely explicable by means of Baeyer's formula. The production of pinic acid, which certainly has the constitution assigned to it by Baeyer (Abstr., 1896, i, 247), is attributed to profound internal change.

A. L.

**Condensation of Acetaldehyde with Propaldehyde.** By F. X. SCHMALZHOFFER (*Monatsh.*, 1900, 21, 671—692. Compare Lieben and Zeisel, Abstr., 1886, 783).—The aldol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHO}$ , obtained when a mixture of acetaldehyde and propaldehyde is heated in a sealed vessel with potassium hydrogen carbonate solution, forms a colourless liquid distilling at  $92^\circ$  under 20 mm. pressure; it is appreciably soluble in water and readily in alcohol or ether; when kept for some time, it polymerises to  $(\text{C}_5\text{H}_{10}\text{O}_2)_2$ , and on continued boiling in a reflux apparatus it loses the elements of water and yields tiglic aldehyde. The aldol yields an *acetyl* derivative,



which distils at  $105\text{--}110^\circ$  under reduced pressure, and on reduction yields 1:2-dimethylpropan-1:3 diol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$ , which distils at  $200^\circ$  under atmospheric pressure or at  $112\text{--}115^\circ$  under 20 mm. pressure; its *diacetyl* derivative,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OAc}$ , distils at  $107\text{--}108^\circ$  under 18 mm. pressure. When heated with dilute sulphuric acid, the glycol is converted into methylethylacetaldehyde and the *anhydride*  $(\text{C}_5\text{H}_{10}\text{O})_2$ , distilling at  $180\text{--}185^\circ$  under atmospheric pressure. On oxidation with 1 per cent. permanganate, the glycol yields  $\beta$ -hydroxy- $\alpha$ -methylbutyric acid (compare Rücker, *Ber.*, 1877, 10, 1754), and the aldol when oxidised in a similar manner yields methyl ethyl ketone. Attempts to obtain the oxime of the aldol gave the *oxime* of tiglic aldehyde as an oil distilling at  $150\text{--}154^\circ$  under 20 mm. pressure.

J. J. S.

**Boiling Points of Mixtures of Chloral and Water.** By JOSEPH C. CHRISTENSEN (*J. Physical Chem.*, 1900, 4, 585—597).—Tables and curves are given for the boiling points of mixtures of chloral and water, several sets of experiments being recorded. The boiling point of the chloral falls rapidly on addition of water, attaining a minimum for about 4 per cent. of water, it then rises at first very rapidly, but slowly after about 20 per cent. of water has been reached. The readings are, however, only given for the Beckmann thermometer, the actual temperatures not being recorded, whilst no determinations appear to have been made in the neighbourhood of the minimum.

L. M. J.

**Nomenclature of the Peroxides: Aldehydic Peroxides.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 2479—2487).—The authors suggest that hydrogen peroxide, its acyl derivatives, and their peroxides should be called "hydroperoxide," "peracids," and "peroxides" respectively. Accordingly, the compound  $\text{Ph}\cdot\text{CO}\cdot\text{O}_2\text{H}$  is "benzoicperacid," and its anhydride "benzoicperoxide." The term "persulphuric acid" is retained for the substance  $(\text{HSO}_4)_2$  and Caro's acid,  $\text{HSO}_3\cdot\text{O}_2\text{H}$ , is called monosulphoperacid. The paper contains a



list of the peroxides with their designations according to the proposed nomenclature.

*Dichloral peroxide hydrate*,  $O_2[CH(OH) \cdot CCl_3]_2$ , obtained by treating chloral either with an ethereal solution of hydrogen peroxide or with Caro's reagent, crystallises from benzene or chloroform in hexagonal leaflets or plates and melts at  $122^\circ$ ; it is freely soluble in ether, forming a compound containing 1 mol. of the solvent, which crystallises in long prisms. The dry substance, when mixed with potassium iodide, evolves oxygen, a small amount of iodine being simultaneously liberated; it is decomposed by a solution of sodium hydrogen carbonate into chloral and hydrogen peroxide.

The pungent explosive substances produced either by treating diethyl or dipropyl ketone with Caro's reagent, or by decomposing diacetone diperoxide with concentrated sulphuric acid, are not simple ketone peroxides as previously stated (this vol., i, 206, 328); they are 'per-acids' produced by oxidation either from the ketones or from the acetic acid employed as solvent.

Acetaldehyde becomes peroxidised when treated with a sulphuric acid solution of hydrogen peroxide, and yields an oily product which subsequently solidifies; the oil is probably a diacetaldehyde peroxide hydrate and the solid a diacetaldehyde peroxide; this point has not, however, been definitely settled, owing to the explosive nature of the compounds.

*Dibenzaldehydiperoxide*,  $C_{14}H_{12}O_4$ , produced by adding benzaldehyde to a dilute alcoholic solution of hydrogen peroxide and sulphuric acid, crystallises in prisms or needles and decomposes at  $202^\circ$ ; it dissolves in the ordinary organic solvents but is insoluble in water. This substance is the inner anhydride,  $CHPh \begin{smallmatrix} O \cdot O \\ \diagup \quad \diagdown \\ O \cdot O \end{smallmatrix} CHPh$ , of the compound,  $O_2(CHPh \cdot OH)_2$ , obtained by Nef by the action of hydrogen peroxide alone on benzaldehyde (Abstr., 1898, i, 109). Hexamethylenetriperoxidetriamine (hexahydroxymethylenetriamine, Legler, Abstr., 1886, 327) is conveniently prepared by adding 40 per cent. aldehyde to a solution of ammonium sulphate in commercial hydrogen peroxide at  $55^\circ$ ; this substance results from the action of ammonia on diformaldehyde peroxide hydrate,  $OH \cdot CH_2 \cdot O \cdot O \cdot CH_2 \cdot OH$ , the constitutional formula,  $N:(CH_2 \cdot O \cdot O \cdot CH_2)_3:N$ , indicating its mode of formation.

G. T. M.

**Semi-Aldehyde of Malonic Acid.** By ALFRED WOHL and W. EMMERICH (*Ber.*, 1900, 33, 2760—2764).—When digested with very dilute alkali hydroxide solution,  $\beta$  chloropropaldehydediethylacetal gives rise to  $\beta$ -hydroxypropaldehydediethylacetal, which, on oxidation with potassium permanganate, yields  $\beta$ -diethoxypropionic acid. When the concentrated aqueous solution of the potassium salt of this acid is gently warmed with excess of sulphuric acid, the two ethoxy-groups are replaced by an oxygen atom, the resulting compound being the semi-aldehyde of malonic acid (aldehydopropionic acid), which was not obtained in sufficient quantity to allow of its boiling point being determined.

*$\beta$ -Hydroxypropaldehydediethylacetal*,  $OH \cdot CH_2 \cdot CH_2 \cdot CH(OEt)_2$ , is a

colourless oil boiling at  $98^{\circ}$  under 20 mm., and at  $118^{\circ}$  under 36 mm. pressure.

*Methyl  $\beta$ -diethoxypropionate*,  $\text{CH}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , is a colourless oil which boils undecomposed at  $193^{\circ}$  and dissolves slightly in water.

T. H. P.

**Fermentation of Pentoses.** By ERNST L. SALKOWSKI (*Zeit. physiol. Chem.*, 1900, 30, 478—494).—On subjecting xylose and arabinose to putrefactive decomposition, the main products are volatile fatty acids. In the case of arabinose, alcohol is formed as well; in the case of xylose, this does not occur.

W. D. H.

**Nature of Inactive Sorbose.** By J. H. ADRIANI (*Rec. Trav. Chim.*, 1900, 19, 183—185).—*d*-Sorbose has a rotatory power  $[\alpha]_D + 41.8^{\circ}$  in a saturated 85 per cent. alcoholic solution, and 10 c.c. of the solution contains 0.1713 gram of the compound. A saturated solution of *i*-sorbose in 85 per cent. alcohol contains 0.1223 gram of substance per 10 c.c. When two mixtures of 0.4 gram of *i*-sorbose with 0.5 gram and 0.8 gram respectively of *d*-sorbose are separately treated with 30 c.c. of 85 per cent. alcohol, the two saturated solutions obtained have practically identical rotatory powers and concentrations. From these results, it is concluded that *i*-sorbose is a racemic compound and does not consist of inactive mixed crystals.

N. L.

**Solubility of Lime in Saccharine Solutions.** By JULIUS WEISBERG (*Bull. Soc. Chim.*, 1900, [iii], 23, 740—745. Compare Abstr., 1899, ii, 748).—The solubility in sugar solutions of different strengths of lime in the three forms of calcium oxide, calcium hydroxide, and milk of lime was determined at  $15$ — $16^{\circ}$ , and the results are given in tabular form. The solubilities are in each case sensibly greater than has been found by previous observers. Of the three forms of lime, calcium oxide is the most, and milk of lime the least, soluble; solutions of the former contain about 28 parts of calcium oxide per 100 parts of sugar, but it is possible to obtain somewhat more concentrated, although unstable, solutions. All the solutions become gelatinous, or deposit lime, on heating, and again become clear on cooling. The results of some preliminary experiments on the solubility of lime in sugar solutions at  $80^{\circ}$  and  $90^{\circ}$  are also recorded and compared with Lamy's figures.

N. L.

**Trehalose.** By IWAN SCHUKOFF (*Zeit. Ver. deut. Zuckerind.*, 1900, 818—823).—When crystallised from water, trehalose ( $+ \text{H}_2\text{O}$ ) begins to soften at  $94^{\circ}$  and melts completely at  $96.5$ — $97.5^{\circ}$ . It forms compounds with lime,  $2\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{CaO}$ , and strontia,  $2\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{SrO}$ . Oxidation with nitric acid of sp. gr. 1.15 yields saccharic acid. Baumann's method of benzylation yields a mixture of *tri*- and *tetra*-benzoyltrehalose, whilst by Panormoff's modification of this method, *hepta*- and *octo*-benzoyltrehalose are obtained; all these compounds are readily hydrolysed by normal alcoholic potash.

T. H. P.

**Oxycelluloses of Cotton, Flax, Hemp, and Rhea.** By LÉO VIGNON (*Compt. rend.*, 1900, 131, 558—560).—Purified cotton, flax, hemp, and rhea-fibre, when treated with potassium chlorate and hydro-

chloric acid, yield almost the same proportion (70 per cent.) of oxycellulose, and the four oxycelluloses thus obtained are practically identical in reducing power and acidic properties with respect to colouring matters such as safranin and methylene-blue, and seem to yield the same osazone. The comparatively small differences observed may be attributed to different degrees of condensation of the  $(C_6H_{10}O_5)_n$  molecule, but in other respects the four celluloses seem to be identical.

C. H. B.

**Acetyl Derivatives of Cellulose and Oxycellulose.** By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1900, 131, 588—590).—The action of acetic anhydride in presence of zinc chloride on purified cotton, and on the oxycellulose prepared from it, yields a tetracetyl derivative which seems to be mixed with some triacetyl derivative. A large quantity of tarry products is, however, formed at the same time, and hence the evidence as to the existence of four hydroxyl groups in cellulose and oxycellulose is not conclusive.

C. H. B.

**Reduction of Nitrocelluloses.** By LÉO VIGNON (*Compt. rend.*, 1900, 131, 530—532).—When nitrocelluloses and nitro-oxycelluloses are reduced by ferrous chloride, the nitro-group is eliminated, but the aldehyde group is not affected. The nitrocelluloses yield oxycellulose, and this affords further proof that they are really nitro-oxycelluloses (this vol., i, 589). On the other hand, when nitrocelluloses and nitro-oxycelluloses are reduced with ammonium sulphide, the aldehyde group is reduced as well as the nitro-group. The difference between the two reductions is probably due to the fact that the first takes place in presence of an acid and the second in presence of an alkali.

C. H. B.

**Action of Silver Oxide on Bromoamines with Tertiary Amino-Groups.** By NIC. M. KJERNER (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 381—385).—The action of silver oxide on *aa*-trimethylheptyl-dibromoamine (di-*iso*amyl-dibromoamine),  $CHMe_2 \cdot [CH_2]_1 \cdot CMe_2 \cdot NBr_2$ , yields acetic acid and an unsaturated hydrocarbon probably having the formula  $CHMe_2 \cdot [CH_2]_3 \cdot CH \cdot CMe_2$ . Under similar conditions, the dibromo-derivative of the amine obtained by reducing nitrohexanaphthene (see Markownikoff, *Abstr.*, 1899, i, 22) yields an unsaturated hydrocarbon and a bromo-compound boiling at 160—170°.

T. H. P.

**Action of Zinc Alkyls on Nitrous Esters and Nitroparaffins.** By IWAN I. BEWAD (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 420—454; 455—542).—The action of zinc alkyls on alkyl nitrites and nitroparaffins has been investigated, the conditions of working being as follows: The zinc alkyl (rather more than 2 mols.) was placed in a flask filled with carbon dioxide, ether added, and to the cool solution an ethereal solution of the nitrite or nitro-compound (1 mol.) was added gradually and with continuous shaking. After being left for some time, in some cases several months, during the first portion of which the liquid was kept cool, water was added and the decomposition products studied. For the alkyl nitrites, these products are: Zinc hydroxide; the paraffin corresponding with the radicle of the

zinc alkyl; two alcohols corresponding with the two radicles of the zinc alkyl and of the nitrite; and a  $\beta$ -disubstituted hydroxylamine containing as substituent groups the two alkyl radicles of the zinc alkyl.

The action of zinc ethyl on *isopropyl nitrite* yields ethane, ethyl and *isopropyl alcohols*, together with  $\beta$ -*diethylhydroxylamine*,  $\text{NEt}_2 \cdot \text{OH}$ , which is a colourless liquid with a characteristic smell and a caustic taste, and boils at  $132\text{--}132.5^\circ$  under 757 mm. and at  $40.5\text{--}41^\circ$  under 10 mm. pressure; it is slightly soluble in water, but mixes in all proportions with the organic solvents, and has the sp. gr. 0.8853 at  $0^\circ/0^\circ$  and 0.867 at  $20^\circ/0^\circ$ ; it has the normal molecular weight in very dilute benzene solution, and on cooling it solidifies to a crystalline mass which melts at  $-3^\circ$ . The *hydrochloride*,  $\text{C}_4\text{H}_{11}\text{ON} \cdot \text{HCl}$ , melts at  $72\text{--}73^\circ$ , whilst the *hydrobromide* forms hygroscopic crystals melting at  $55\text{--}56.5^\circ$ , and the *hydriodide* crystallises in dendritic growths of prisms melting at  $165\text{--}167^\circ$ ; the *oxalate* melts at  $134\text{--}138^\circ$ . On reduction, the base yields diethylamine, whilst it is oxidised and turned brown in the air; it reduces solutions of the heavy metals in the cold and itself suffers oxidation, yielding, when copper sulphate is employed, acetaldehyde, ammonia, ethylamine, and diethylamine.

The action of water on the product of the interaction of zinc ethyl and *isoamyl nitrite* yields compounds analogous to the above reaction, and, in addition ethyl *isoamyl ether* and  $\beta$ -ethylhydroxylamine (?).

$\beta$ -*Dipropylhydroxylamine*,  $\text{NPr}_2 \cdot \text{OH}$ , obtained from zinc propyl and propyl nitrite, forms colourless plates melting at  $28.5\text{--}29.5^\circ$ , and boiling at  $157\text{--}159^\circ$  under 748 mm. and at  $69\text{--}70^\circ$  under 17–20 mm. pressure; it has a characteristic odour and a caustic taste, and is only slightly soluble in water, but dissolves in all proportions in the organic solvents. On reduction, it yields dipropylamine, whilst oxidation by means of copper sulphate gives propaldehyde, ammonia, propylamine, and dipropylamine. The *hydrochloride* forms a light, non-hygroscopic, crystalline powder melting at  $87\text{--}88^\circ$ , the *hydrobromide* a crystalline powder melting at  $74\text{--}75^\circ$ , and the *hydriodide* hygroscopic, colourless needles or plates.

In the case of the nitro-paraffins, the products obtained by the action of zinc alkyls are: zinc hydroxide; the paraffin and the alcohol corresponding with the radicle of the zinc compound; a nitroparaffin formed from the one used in the reaction by the substitution of the alkyl of the zinc compound for a hydrogen atom; a disubstituted  $\beta$ -hydroxylamine containing two different radicles, one being that of the zinc alkyl and the other a primary, secondary, or tertiary radicle containing as many carbon atoms in the molecule as are present in the nitroparaffin and the radicle of the zinc compound together.

Nitroethane and zinc ethyl give rise to *sec.*nitrobutane, a neutral compound which boils at  $180\text{--}181^\circ$ , and has the sp. gr. 1.1741 at  $0^\circ/0^\circ$ , ethyl alcohol and  $\beta$ -ethyl*sec.*butylhydroxylamine,  $\text{CHMeEt} \cdot \text{NEt} \cdot \text{OH}$ , which is a colourless, viscous liquid with a characteristic odour and a caustic taste; it boils at  $155\text{--}158^\circ$  under 756 mm. and at  $57\text{--}58^\circ$  under 8 mm. pressure, and has the sp. gr. 0.892 at  $0^\circ/0^\circ$  and 0.8757 at  $20^\circ/0^\circ$ ; it is only slightly soluble in water, but dissolves in all proportions in the organic solvents. On reduction, it yields ethyl*sec.*-

butylamine, and on oxidation with ferric chloride or copper sulphate in the cold it gives acetaldehyde, ammonia, methyl ethyl ketone and ethylsec.butylamine. The *hydrochloride* is hygroscopic and melts at  $56-57^{\circ}$ ; the *oxalate* crystallises in nodular aggregates melting at  $114-114.5^{\circ}$ , and the *acid oxalate* melts at  $93-95^{\circ}$ .

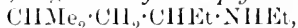
$\beta$ -Ethylsec.amylhydroxylamine,  $\text{CHEt}_2\cdot\text{NEt}\cdot\text{OH}$ , obtained together with  $\alpha$ -nitropropane, &c., from zinc ethyl and nitropropane, is a viscous liquid with a characteristic smell and a caustic taste, and dissolves in all proportions in the organic solvents, but only to a slight extent in water; it boils at  $167-170^{\circ}$  under 756 mm., and at  $65-67^{\circ}$  under 8 mm. pressure, and has the sp. gr. 0.8903 at  $0^{\circ}/0^{\circ}$  and 0.8744 at  $20^{\circ}/0^{\circ}$ ; on cooling, it solidifies to a crystalline mass melting at  $-8^{\circ}$ . On reduction, it yields ethylsec.butylamine, whilst oxidation with ferric chloride converts it into acetaldehyde, ammonia, diethyl ketone, sec.amylamine and ethylsec.amylamine. The *hydrochloride* of the base forms hygroscopic crystals, and the *hydriodide* a pale yellow, crystalline powder; the *oxalate* melts at  $118-119^{\circ}$ .

$\beta$ -Ethyltert.amylhydroxylamine,  $\text{CMe}_2\text{Et}\cdot\text{NEt}\cdot\text{OH}$ , prepared from zinc ethyl and nitroisopropane, is a thick, colourless liquid which boils at  $156-160^{\circ}$  under 760 mm. and at  $58.5-60.5^{\circ}$  under 12 mm. pressure and does not solidify when cooled to  $-80^{\circ}$ ; its sp. gr. at  $0^{\circ}/0^{\circ}$  is 0.8912. On reduction, it yields ethyltert.amylamine, which is also formed on oxidation together with tert.amylamine and  $\beta\beta$ -nitroso-methylbutane. The *hydrochloride* of the base melts at  $83^{\circ}$ .

$\beta$ -Ethylsec.heptylhydroxylamine,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{NEt}\cdot\text{OH}$ , obtained by the action of zinc ethyl on the nitropentane,



is a viscous liquid which boils at  $91.5-93.5^{\circ}$  under 12-13 mm. pressure, and has the sp. gr. 0.8797 at  $0^{\circ}/0^{\circ}$  and 0.8641 at  $20^{\circ}/0^{\circ}$ . On reduction or oxidation, it gives ethylsec.heptylamine,



which boils at  $155-158^{\circ}$ , and forms a *hydrochloride* melting at  $92-97^{\circ}$  and a pale yellow *benzenesulphonamide*. Other products of the oxidation are acetaldehyde, ethyl isobutyl ketone, and traces of isovaleric acid. The *hydrochloride*, which is very hygroscopic and melts at  $66-74^{\circ}$ , and the *hydrobromide* of the hydroxylamine were prepared.

$\beta$ -Ethylpropylhydroxylamine,  $\text{NEtPr}\cdot\text{OH}$ , prepared from zinc ethyl and nitromethane, is a viscous liquid similar to, but with a less caustic taste than, its higher homologues; it boils at  $143-147^{\circ}$  under 765 mm. and at  $57-58^{\circ}$  under 10-11 mm. pressure, and has a sp. gr. 0.8778 at  $0^{\circ}/0^{\circ}$ . Its *hydrochloride* melts at  $55-58^{\circ}$ . The usual products were obtained on oxidation and on reduction.

$\beta$ -Propylsec.amylhydroxylamine,  $\text{CHMePr}\cdot\text{NPr}\cdot\text{OH}$ , prepared from zinc propyl and nitroethane, boils at about  $183^{\circ}$  under the ordinary pressure, and at  $90.5-92^{\circ}$  under 16 mm., and has the sp. gr. 0.8807 at  $0^{\circ}/0^{\circ}$  and 0.8654 at  $20^{\circ}/0^{\circ}$ . Its *hydrochloride* is very hygroscopic and melts at  $63-65^{\circ}$ . The normal oxidation products were obtained.

$\beta$ -Propylsec.hexylhydroxylamine,  $\text{CHEtPr}\cdot\text{NPr}\cdot\text{OH}$ , obtained by the action of zinc propyl on nitropropane, boils at about  $185^{\circ}$  under the ordinary pressure and at  $95-97^{\circ}$  under 14 mm., and has the sp. gr. 0.8815 at  $0^{\circ}/0^{\circ}$  and 0.8637 at  $20^{\circ}/0^{\circ}$ . The products of oxidation,

reduction and of the action of sodium on it were studied. The *hydrochloride* melts at 52—54°, and the *hydrobromide* at 44—45°.

*β-Propyltert.hexylhydroxylamine*,  $\text{CMe}_2\text{Pr}\cdot\text{NPr}\cdot\text{OH}$ , prepared from zinc propyl and nitroisopropane, is lighter than water and boils at 74—77° under 7—8 mm. pressure. The *hydrochloride* melts at 77—81°.

*β-tert.Heptylhydroxylamine*,  $\text{C}_6\text{H}_{13}\cdot\text{NH}\cdot\text{OH}$ , obtained by the action of zinc ethyl on chloropicrin, separates from the solution of its hydrochloride as a colourless, microcrystalline powder, melting at 68·5—69·5° and boiling under the ordinary pressure at about 185°; it has a characteristic smell and dissolves slightly in water, and in all proportions in benzene or ether; the *hydrochloride* forms prismatic crystals melting at 146—146·5°. On reduction, it yields *tert.heptylamine* [ $\gamma\gamma$ -aminoethylpentane].

The action of zinc ethyl on nitrobenzene gives rise to aniline. With the zinc alkyls, therefore, tertiary nitro-compounds give products different from those obtained with primary or secondary nitro-paraffins; in the former case, either a  $\beta$ -monoalkylhydroxylamine or an amine is formed, whilst in the latter  $\beta$ -dialkylhydroxylamines are always obtained.

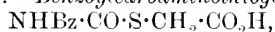
T. H. P.

**New Derivative of Glycine.** By LUIGI BALBIANO and D. TRACIATTI (*Ber.*, 1900, 33, 2323—2326).—When a mixture of glycine and glycerol is heated in a sealed tube at 150—170° for 24—30 hours, ammonia and a yellow, amorphous compound,  $\text{C}_{22}\text{H}_{34}\text{O}_{13}\text{N}_{10}$ , are formed; the latter carbonises at 250° and, when hydrolysed with hydrochloric acid, yields glycine and glycollic acid.

R. H. P.

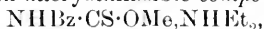
**Behaviour of Acylthioncarbamic Esters with Alkyl Iodides and Amines; Benzoyliminothiocarbamic Esters, Acyclic Benzoylpseudocarbamides and Benzoylcarbamides.** By HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1900, 24, 189—221).—*Methyl acetylthioncarbamate*,  $\text{NHAc}\cdot\text{CS}\cdot\text{OMe}$ , obtained by treating acetyl chloride with lead or potassium thiocyanate and boiling the product with methyl alcohol, or more easily by the action of acetic anhydride on methyl thioncarbamate, crystallises from light petroleum, melts at 79—80°, and is readily soluble in water, alcohol, benzene, or chloroform; when boiled with freshly precipitated mercuric oxide, the sulphur is eliminated. If this compound is left for three weeks in contact with methyl iodide at 40—45°, it is converted into *methyl acetylthiolcarbamate*,  $\text{NHAc}\cdot\text{CO}\cdot\text{SMe}$ , which crystallises from benzene in fine needles, melts at 145·5—146°, and is easily soluble in hot water or alcohol; the sulphur is not removed by the action of mercuric oxide. *Ethyl acetylthioncarbamate*,  $\text{NHAc}\cdot\text{CS}\cdot\text{OEt}$ , crystallises from water in prisms, melts at 100—101°, and dissolves readily in alcohol or benzene and sparingly in water; it cannot be converted into the isomeric thiol compound, but when heated at 80—90°, yields ethyl thiolcarbamate. Methyl and ethyl benzoylthioncarbamates may be prepared by treating the product of the action of benzoyl chloride on potassium thiocyanate with alcohol. When methyl benzoylthioncarbamate is heated with methyl iodide at 80—90° for 6 hours in a sealed tube, it yields *methyl benzoylthiolcarbamate*,  $\text{NHBz}\cdot\text{CO}\cdot\text{SMe}$ , which crystallises

in long prisms, melts at  $152-153^{\circ}$ , and is not affected by mercuric oxide; if, however, the mixture is heated at  $100-110^{\circ}$ , decomposition occurs, and a nitrogenous compound free from sulphur is produced, melting at  $215^{\circ}$ , and crystallising from alcohol in small needles. Ethyl benzoylthioncarbamate shows little, if any, tendency to undergo a molecular rearrangement with ethyl iodide, but if heated with it, benzamide is produced. *Benzoylcarbaminothioglycollic acid*,



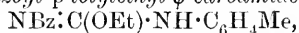
obtained by the action of chloroacetic acid on methyl benzoylthioncarbamate, crystallises in colourless needles, melts at  $169-170^{\circ}$ , and is not changed when heated with mercuric oxide; if treated with ammonia, it yields benzoylcarbamide melting at  $214-215^{\circ}$ . *Methyl dibenzoylthioncarbamate*,  $\text{NBz}_2 \cdot \text{CS} \cdot \text{OMe}$ , formed by the action of benzoic anhydride on the sodium salt of methyl benzoylthioncarbamate, crystallises from light petroleum in colourless plates, melts at  $81-82^{\circ}$ , and reacts with phenylhydrazine to form hydrogen sulphide and benzoylphenylhydrazine. By the action of methylene iodide on ethyl thioncarbamate, *methylene thiolcarbamate*,  $\text{CH}_2(\text{S} \cdot \text{CO} \cdot \text{NH}_2)_2$ , is produced, melting at  $168-170^{\circ}$ . Ethylene thiolcarbamate (Wheeler and Barnes, Abstr., 1899, i, 798) melts at  $231-232^{\circ}$ . *Trimethylene thiolcarbamate*,  $\text{CH}_2(\text{CH}_2 \cdot \text{S} \cdot \text{CO} \cdot \text{NH}_2)_3$ , from trimethylene bromide and ethyl thioncarbamate, crystallises from hot water in plates, melts at  $177-179^{\circ}$ , and dissolves readily in alcohol but only sparingly in benzene. If isobutylene bromide is allowed to react with ethyl thioncarbamate, cyanuric acid and ethyl thiolcarbamate are obtained.

When ethyl benzoylthioncarbamate is dissolved in alcoholic ammonia, hydrogen sulphide and benzoyl- $\psi$ -ethylcarbamide are produced; the last-mentioned substance is converted by dilute hydrochloric acid into benzoylcarbamide, and it furnishes an *aurichloride* which melts at  $140^{\circ}$ . Methyl benzoylthioncarbamate unites with diethylamine to form an uncrystallisable compound,



which dissolves readily in alcohol or benzene, and is precipitated as an oil by light petroleum. Ethyl benzoylthioncarbamate combines similarly with diisobutylamine, and if the product is heated, hydrogen sulphide, mercaptan, and alcohol are produced, together with a thick oil; when this oil is treated with hydrochloric acid, it yields ethyl chloride and *benzoyldiisobutylthiocarbamide*,  $\text{NHBz} \cdot \text{CS} \cdot \text{N}(\text{C}_4\text{H}_9)_2$ , which crystallises from alcohol in prisms and melts at  $130-132^{\circ}$ ; if, however, the oil is distilled under 25 mm. pressure, a fraction is obtained boiling at  $288-311^{\circ}$  under the ordinary pressure, which when rendered alkaline and extracted with ether, furnishes *diisobutylbenzamide* crystallising in prisms and melting at  $65^{\circ}$ . Methyl benzoylthioncarbamate and diisobutylamine unite to form a substance,  $\text{NHBz} \cdot \text{CS} \cdot \text{OMe}, \text{NH}(\text{C}_4\text{H}_9)_2$ , which melts at  $55-60^{\circ}$ , is extremely soluble in benzene or alcohol, and is decomposed by heat with production of hydrogen sulphide, mercaptan, and benzamide. Ethyl benzoylthioncarbamate reacts with benzylamine to form hydrogen sulphide, mercaptan, and *benzoylbenzylcarbamide*,  $\text{NHBz} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}$ , melting at  $89^{\circ}$ ; it behaves similarly with aniline, benzoylphenylcarbamide being produced. When a mixture of ethyl benzoylthion-

carbamate and *p*-toluidine in molecular proportion is heated on the water-bath, hydrogen sulphide is evolved, and an oil obtained which consists chiefly of *benzoyl-p-tolylethyl-ψ-carbamide*,

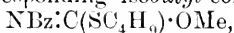


and when exposed to the air yields *benzoyl-p-tolylcarbamide*,  $\text{NHBz}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , melting at  $80-81^\circ$ . If ethyl acetylthioncarbamate is warmed with *p*-toluidine, the products are hydrogen sulphide, *p*-acetyltoluidine, and an oil which was not examined. When ethyl benzoylthioncarbamate is heated with 2:4-dimethylaniline, it furnishes hydrogen sulphide, mercaptan, and *αβ-benzoyl-m-xyllylcarbamide*,  $\text{NHBz}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2$ , which melts at  $215-217^\circ$ . Ethyl benzoylthioncarbamate and *p*-anisidine react with formation of hydrogen sulphide, benzoyl-*p*-anisidine, and *benzoyl-p-methoxyphenylcarbamide*,  $\text{NHBz}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , melting at  $216-218^\circ$ , together with small quantities of an oil which, on treatment with hydrochloric acid, yields ethyl chloride, thus indicating the presence of benzoyl-ethyl-*p*-methoxyphenyl-*ψ*-carbamide. By the action of *α*-naphthylamine on methyl benzoylthioncarbamate, hydrogen sulphide is evolved, and an oil produced which furnishes *benzoyl-α-naphthylcarbamide*, melting at  $165-166^\circ$ . When methyl benzoylthioncarbamate is warmed with *β*-naphthylamine, hydrogen sulphide is formed, together with an oil which yields benzoyl-*β*-naphthalide. Ethyl benzoylthioncarbamate and diphenylamine react with formation of hydrogen sulphide and an oil, which is decomposed by hydrogen chloride with separation of diphenylamine. When an ethereal solution of ethyl benzoylthioncarbamate and *o*-phenylenediamine is evaporated, the products are hydrogen sulphide and *dibenzoylphenylenedicarbamide*,  $\text{C}_6\text{H}_4(\text{NH}\cdot\text{CO}\cdot\text{NHBz})_2$ , which melts at  $235^\circ$ . By the action of phenylhydrazine on methyl benzoylthioncarbamate, hydrogen sulphide is evolved and 3-ethoxy-1:5-diphenyltriazole obtained in colourless needles; this melts at  $85-86^\circ$ , and when heated with hydrochloric acid yields 1:5-diphenyl-3-triazolone. Ethyl acetylthioncarbamate reacts with phenylhydrazine to form hydrogen sulphide and 3-ethoxy-1-phenyl-3-methyltriazole, which crystallises in long prisms and melts at  $49-50^\circ$ .

The benzoyliminothiocarbonic esters are readily formed by the action of alkyl iodides on the sodium or potassium salts of the benzoylthioncarbamic esters, and are always obtained as oils. When the potassium salt of ethyl benzoylthioncarbamate is treated with ethyl iodide, diethyl benzoyliminothiocarbonate is produced as a colourless oil which boils at  $209-212^\circ$  under 19 mm. pressure; this substance was first prepared by Lössner (Abstr., 1875, 641). The *dimethyl* compound,  $\text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{OMe}$ , similarly produced, is converted by dry hydrogen chloride into methyl benzoylthiolcarbamate, whilst by the action of hydrogen sulphide the corresponding thioncarbamate is formed. *Benzoyliminomethylthiolethylcarbonate*,  $\text{NBz}\cdot\text{C}(\text{SEt})\cdot\text{OMe}$ , boils at  $210^\circ$  under 20 mm. pressure; it reacts with hydrogen chloride with formation of methyl chloride and *ethyl benzoylthiolcarbamate*,  $\text{NHBz}\cdot\text{CO}\cdot\text{SEt}$ , which crystallises in long, slender prisms, and melts at  $105-107^\circ$ ; on attempting to prepare the last-mentioned substance by warming ethyl thiolcarbamate with benzoic anhydride, cyanophenine is produced, together with a compound



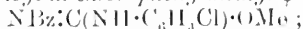
which crystallises in needles, melts at 167—168°, and is probably the polymeric modification of ethyl benzoylthioncarbamate described by Miquel (*Ann. Chim. Phys.*, 1877, [v], 11, 269). When *benzoylimino-methylthiolisopropylcarbonate*,  $\text{NBz:C}(\text{SPr}^\beta)\cdot\text{OMe}$ , is treated with hydrochloric acid, *isopropyl benzoylthiolcarbamate*,  $\text{NHBz}\cdot\text{CO}\cdot\text{SPr}^\beta$ , is obtained which crystallises in prisms and melts at 136—137°. In the same way, the corresponding *isobutyl* compound,



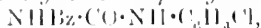
furnishes *isobutyl benzoylthiolcarbamate*,  $\text{NHBz}\cdot\text{CO}\cdot\text{SC}_4\text{H}_9$ , which crystallises in plates and melts at 115—117°; on the other hand, the *isoamyl* compound,  $\text{NBz:C}(\text{SC}_5\text{H}_{11})\cdot\text{OMe}$ , yields *methyl benzoylthioncarbamate*.

Benzoyliminothiocarbonic esters readily react with amines to form benzoyl- $\psi$ -carbamide ethers, which, when treated with hydrochloric acid, are in most cases quantitatively converted into the corresponding benzoylcarbamides. By the action of alcoholic ammonia on benzoyliminomethylthiolisopropylcarbonate, *isopropyl mercaptan* and benzoylmethyl- $\psi$ -carbamide are obtained; the latter compound is identical with that described by Dixon (*Trans.*, 1899, 75, 381), and yields benzoylcarbamide when warmed with hydrochloric acid. *Benzoylmethylethyl- $\psi$ -carbamide*,  $\text{NBz:C}(\text{NHEt})\cdot\text{OMe}$ , obtained as an oil by the action of ethylamine on benzoyliminomethylthiolisopropylcarbonate, is similarly converted into  $\alpha\beta$ -benzoylethylcarbamide, which melts at 114°. When *isobutylamine* is mixed with benzoyliminomethylthioethylcarbonate, a vigorous action ensues with production of ethyl mercaptan and an oil which yields *benzoylisobutylcarbamide*,  $\text{NHBz}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_4\text{H}_9$ ; the last-mentioned compound crystallises in long, slender prisms and melts at 115°. When benzoyliminothioethylethylcarbonate and diisoamylamine are warmed together until evolution of mercaptan ceases, and the product submitted to the action of hydrogen sulphide, benzonitrile and benzamide are formed, but no appreciable amount of diisoamylthionmethylethylcarbamate is obtained. *Benzoylphenylmethyl- $\psi$ -carbamide*,  $\text{NBz:C}(\text{NHPh})\cdot\text{OMe}$ , prepared by the action of aniline on benzoyliminomethylthioethylcarbonate, is converted by hydrochloric acid into benzoylphenylcarbamide. *Benzoylphenylethyl- $\psi$ -carbamide*,  $\text{NBz:C}(\text{NHPh})\cdot\text{OEt}$ , is a pale yellow oil.

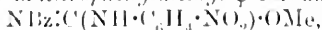
*m*-Chloroaniline reacts with benzoyliminomethylthioethylcarbonate with formation of *benzoyl-m-chlorophenylmethyl- $\psi$ -carbamide*,



this compound yields *benzoyl-m-chlorophenylcarbamide*,



which crystallises in colourless needles, melts at 200°, and can also be prepared by the action of *m*-chloroaniline on benzoylethylthioncarbamate. *Benzoyl-m-nitrophenylmethyl- $\psi$ -carbamide*,



results from the action of *m*-nitroaniline on benzoyliminomethylthioethylcarbonate; it furnishes *benzoyl-m-nitrophenylcarbamide*,



which crystallises in needles and melts at 231—232°. *Benzoyl- $\psi$ -methyl- $\psi$ -cumylcarbamide*,  $\text{NBz:C}(\text{NH}\cdot\text{C}_6\text{H}_2\text{Me})\cdot\text{OMe}$ , is readily

formed on warming benzoyliminothiolmethylcarbonate with  $\psi$ -cumidine; *benzoyl- $\psi$ -cumylcarbamide* crystallises from chloroform in long needles and melts at  $207^{\circ}$ . Benzoyliminomethylthiolisobutylcarbonate and methylaniline react slowly with evolution of mercaptan and formation of a purple-coloured oil. E. G.

**Salts of Uric Acid.** By FRANCIS W. TUNNICLIFFE and OTTO ROSENHEIM (*Chem. Centr.*, 1900, [ii], 626; from *The Lancet*).—The so-called quadriurates,  $C_5H_4O_3N_4M', C_5H_3O_3N_4$ , are mixtures of uric acid with its salts. E. W. W.

**3-Ethyluric Acid.** By E. FRANKLAND ARMSTRONG (*Ber.*, 1900, 33, 2308—2314. Compare E. Fischer, *Abstr.*, 1899, i, 458, and this vol., i, 417).—*Ethyl- $\psi$ -uric acid*,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{Et}$ , obtained by the action of ethylcarbimide on uramil in the presence of sodium hydroxide, crystallises from a large quantity of hot water in small, colourless, slender needles, and forms a characteristic *potassium hydrogen* salt, which crystallises in reddish needles, and easily soluble colourless alkali salts, of which the *sodium* (slender needles), *potassium* (large prisms), and *ammonium* (small needles) salts are described. *3-Ethyluric acid*, obtained when the  $\psi$ -acid is treated with hydrochloric acid, crystallises in leaflets or long, prismatic needles which do not melt below  $350^{\circ}$ , and forms the following easily soluble salts: *potassium* (slender needles), *sodium* (well-formed prisms), *ammonium* (slender needles), *potassium hydrogen* (colourless needles), *calcium* and *barium* salts (both clusters of slender needles); when treated with ethyl iodide, it yields a *diethyluric acid*, which crystallises in long, feathery needles, melts and decomposes at  $314^{\circ}$ , and forms easily soluble neutral alkali salts. *5:7-Dichloro-2-oxy-3-ethylpurine* is obtained when 3-ethyluric acid is heated at  $130$ — $140^{\circ}$  in a sealed tube with a mixture of phosphorus oxychloride and pentachloride, it melts at  $263$ — $266^{\circ}$  (corr.), forms the following colourless soluble salts: *sodium* (slender needles), *potassium* (thin prisms), *ammonium* (plates or needles), *potassium hydrogen* (prisms), and when treated with hydriodic acid and phosphonium iodide yields *iodo-2-oxy-3-ethylpurine*, which crystallises in reddish needles, melts at  $247$ — $248^{\circ}$  (corr.), and when reduced with zinc dust yields *2-oxy-3-ethylpurine*, which crystallises in colourless prisms, melts at  $250$ — $251^{\circ}$  (corr.), and forms a crystalline *hydrochloride*, a *hydriodide*, a characteristic *platinichloride*, which crystallises in yellowish-red prisms, an *aureichloride*, and crystalline *potassium* and *ammonium* salts. R. H. P.

**Explosiveness of a Mixture of Potassium Cyanide and Nitrite.** By J. W. VAN GEUNS (*Rec. Trav. Chim.*, 1900, 19, 186—187).—A mixture of potassium cyanide and nitrite in molecular proportion detonates when heated to about  $450^{\circ}$ . N. L.

**Three Normal Butyltoluenes [Methyl-*n*-butylbenzenes].** By ST. NIEMCZYCKI (*Chem. Centr.*, 1900, ii, 468—469; from *Bull. Acad. Sci. Cracow*, 1900).—The three methylbutylbenzenes prepared by the action of sodium and propyl bromide on *o*-, *m*-, and *p*-xylyl bromides respectively, are colourless liquids and have pleasant odours. Hydro-

carbons boiling above  $300^{\circ}$  are also formed in the reaction. *o*-Methylbutylbenzene boils at  $200-201^{\circ}$ , and has a sp. gr. 0.87135 at  $18.3^{\circ}$  and specific refractive index  $[n]_D$  1.49662. *m*-Methylbutylbenzene boils at  $197-198^{\circ}$ , and has a sp. gr. 0.86354 at  $18.4^{\circ}$  and specific refractive index  $[n]$  1.49315. *p*-Methylbutylbenzene boils at  $198-199^{\circ}$ , has a sp. gr. 0.8618 at  $14.2^{\circ}$ , and specific refractive index  $[n]_D$  1.4912. Kelbe and Baur's *p*-butyltoluene (Abstr., 1884, 301) is not identical with *p*-methyl-*n*-butylbenzene. E. W. W.

**Fluorine Derivatives of Toluene.** By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1900, ii, 667—668; from *Bull. Acad. roy. Belg.*, 1900, 414—431. Compare Abstr., 1899, i, 197).—Antimony fluoride (2 mols.) acts very slowly on benzotrichloride (3 mols.) at the ordinary temperature, but forms eventually an almost theoretical quantity of  $\omega$ -difluorochlorotoluene,  $\text{CPhClF}_2$ , together with small quantities of  $\omega$ -fluoro- $\omega$ -dichlorotoluene,  $\text{CPhCl}_2\text{F}$ , and  $\omega$ -trifluorotoluene,  $\text{CPhF}_3$ . Fluorodichlorotoluene is apparently formed in larger quantity at temperatures below  $10^{\circ}$ . Difluorochlorotoluene is decomposed by water even at the ordinary temperature, yielding benzoic acid, hydrogen chloride, and hydrogen fluoride. By the action of fuming nitric acid on difluorochlorotoluene at a temperature below  $0^{\circ}$ ,  $\omega$ -difluoro- $\omega$ -chloronitrotoluene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CClF}_2$ , together with some *m*-nitrobenzoic acid are formed; a better yield of the former compound and less of the latter is obtained by using a mixture of fuming nitric acid and phosphoric oxide. Difluorochloronitrotoluene is a colourless liquid, boils at  $230^{\circ}$ , has a sp. gr. 1.4638 at  $15^{\circ}$ , 1.4555 at  $21^{\circ}$ , specific refractive index 1.5043 at  $21^{\circ}$ , and is insoluble in water. It is not readily attacked by water or by nitric acid. Difluorochlorotoluene is destroyed by fuming sulphuric acid, but when dissolved in alcohol it is slowly reduced by sodium amalgam, forming  $\omega$ -difluorotoluene,  $\text{CHPhF}_2$ , which cannot, however, be completely freed from difluorochlorotoluene. Difluorotoluene is a colourless liquid, has a pleasant odour, boils at  $133.5^{\circ}$ , and, by the action of a small quantity of concentrated sulphuric acid or of water at  $200^{\circ}$ , is decomposed into benzaldehyde and hydrogen fluoride. By the action of sodium ethoxide, or more slowly by the action of absolute alcohol, difluorotoluene yields ethyl ether, ethyl benzoate, chloroethane, hydrogen fluoride, and hydrogen chloride.  $\omega$ -Fluoro- $\omega$ -dichlorotoluene is a colourless liquid, has a pungent odour, boils at  $178-180^{\circ}$ , has a sp. gr. 1.3138 at  $11^{\circ}$ , specific refractive index  $[n]_D$  1.5180, and is decomposed by concentrated sulphuric acid or by boiling water.

$\omega$ -Fluoro- $\omega$ -dichloronitrotoluene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CCl}_2\text{F}$ , prepared by the action of nitric acid and phosphoric oxide on fluorodichlorotoluene, is a nearly colourless liquid, boils at  $260^{\circ}$ , and has a sp. gr. 1.408 at  $18^{\circ}$ ; it is only slightly attacked by water, but yields nitrobenzoic acid when boiled with nitric acid of sp. gr. 1.50.

By the replacement of fluorine in the group  $\text{CF}_3$  by chlorine, the stability of the compound is diminished, and the chlorine in the fluorochloro-derivative obtained may be replaced by a hydroxyl group, but the product very readily loses hydrogen fluoride. A table giving the boiling points of corresponding chloro- and fluoro derivatives is given. The replacement of one atom of chlorine by fluorine decreases the boiling

point by less than  $44^{\circ}$ , that is, by less than in the case of the corresponding derivatives of fatty hydrocarbons.

E. W. W.

**Simultaneous Formation of Isomeric Substitution Products of Benzene.** By ARNOLD F. HOLLEMAN [and B. R. DE BRUYN] (*Rec. Trav. Chim.*, 1900, **19**, 188—203. Compare Abstr., 1900, i, 387).—The product of the nitration of chlorobenzene at  $0^{\circ}$  consists of 30.1 per cent. of *o*-chloronitrobenzene and 69.9 per cent. of *p*-chloronitrobenzene, whilst at  $-30^{\circ}$  the proportions are 26.9 and 73.1 per cent. respectively. *m*-Chlorobenzoic acid, when nitrated at  $0^{\circ}$ , yields 11.4 per cent. of 3-chloro-2-nitrobenzoic acid and 88.6 per cent. of the 3:5-acid; almost identical results are obtained when the nitration is carried out at  $-30^{\circ}$ , the relative proportions of the two acids being 11.5 and 88.5 per cent. respectively. Since the ortho- and para-positions relatively to the chlorine are unoccupied in both chlorobenzene and *m*-chlorobenzoic acid, the formation of different proportions of the nitro-derivatives in the two cases shows that the directing influence of the chlorine on the nitro-group is modified by the presence of carboxyl.

Full details of the analysis of the products of nitration are given in the paper.

N. L.

**Nitration of *m*-Chlorotoluene.** By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1900, **33**, 2505—2508).—The two *mononitro*-compounds, obtained by treating *m*-chlorotoluene with concentrated nitric acid, yield on reduction 3-chloro-4-toluidine and 5-chloro-2-toluidine; these bases are separated from each other by the fractional crystallisation of their acetyl derivatives.

3-Chloro-4:6-dinitrotoluene, obtained by nitrating *m*-chlorotoluene with nitric and sulphuric acids, forms pale yellow needles and melts at  $91^{\circ}$ ; it is volatile in steam. A *chloronitrotoluidine* [3:4:6 or 3:6:4], results from the partial reduction of the preceding compound with an alcoholic solution of ammonium sulphite; it crystallises from benzene and light petroleum in yellow leaflets and melts at  $120^{\circ}$ ; its *acetyl* derivative melts at  $262^{\circ}$ .

5-Chloro-2:4-tolylenediamine, obtained from the dinitro-compound by complete reduction with tin and hydrochloric acid, crystallises in colourless leaflets readily soluble in water; it melts at  $123^{\circ}$  and gives the metadiamine reaction with nitrous acid. The *monoacetyl* derivative melts at  $170^{\circ}$ ; the diacetyl derivative melts above  $250^{\circ}$  (compare Morgan, *Trans.*, 1900, **77**, 1209).

An additive product,  $C_{17}H_{14}O_4N_3Cl$ , is formed by treating 3-chloro-4:6-dinitrotoluene with  $\alpha$ -naphthylamine and sodium acetate; it crystallises in orange needles and melts at  $98^{\circ}$ .

4:6-Dinitro-3-tolyl- $\alpha$ -naphthylamine is obtained when this reaction is performed in sealed tubes at  $160^{\circ}$ ; it crystallises from dilute acetone in brown needles having a metallic lustre and melts at  $182^{\circ}$ .

4:6-Dinitro-3-tolyl-4'-hydroxyphenylamine, produced in a similar manner from *p*-aminophenol, forms red crystals and melts at  $194$ — $195^{\circ}$ ; it yields a bluish-black colouring matter on heating with sodium sulphide and sulphur.

G. T. M.

**$\alpha\beta$ -Dichlorostyrenes and some Acetylenes.** By FRANZ KUNCKELL and F. GORSCH (*Ber.*, 1900, **33**, 2654—2658).— $\alpha\beta$ -Dichloro-*p*-tolylethyl-

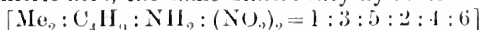
*ene*,  $C_6H_4Me \cdot CCl : CHCl$ , made by heating *p*-tolylchloromethylketone (compare this vol., i, 663) with phosphorus pentachloride on the water-bath, the product being subjected to fractional distillation in a vacuum, forms a yellow oil, with an aromatic odour, which boils at  $245-250^\circ$ , and has a sp. gr. 1.2156 at  $20^\circ$ . *α-Chloro-p-tolylacetylene*,  $C_6H_4Me \cdot C : CCl$ , prepared by heating the foregoing substance with alcoholic potash, is a limpid, aromatic oil which boils at  $145-150^\circ$  under 55 mm. pressure, and has a sp. gr. 1.1142 at  $18^\circ$ .

*p-Tolylacetylene*,  $C_6H_4Me \cdot C : CH$ , is easily prepared by allowing sodium to act on an ethereal solution of *αβ*-dichloro-*p*-methylstyrene, the reaction being completed by warming for an hour at  $40-50^\circ$ ; it has an odour of anise and fennel, forms crystals melting at  $23^\circ$ , boils at  $168-170^\circ$  under atmospheric pressure, and has a sp. gr. 0.912 at  $18^\circ$ .

*αβ*-3-Trichloro-4-methylstyrene,  $C_6H_3MeCl \cdot CCl : CHCl$ , prepared from *o*-chlorotolyl chloromethyl ketone and phosphorus pentachloride, boils at  $270-273^\circ$ , and has a sp. gr. 1.3808 at  $20^\circ$ . *αβ*-Dichloro-2:4-dimethylstyrene,  $C_6H_3Me_2 \cdot CCl : CHCl$ , boils at  $248-249^\circ$ , and has a sp. gr. 1.1648 at  $19^\circ$ . *αβ*-Dichloro-2:5-dimethylstyrene,  $C_6H_3Me_2 \cdot CCl : CHCl$ , boils at  $247-248^\circ$ , and has a sp. gr. 1.1732 at  $18^\circ$ . *p-Xylylchloroacetylene*,  $C_6H_3Me_2 \cdot C : CCl$ , boils at  $134-140^\circ$  under 27 mm. pressure, and has a sp. gr. 1.0743 at  $19^\circ$ .  
A. L.

#### Derivatives of Butylxylene [1:3-Dimethyl-5-butylbenzene].

By ALBERT BAUR-THURGAU (*Ber.*, 1900, 33, 2562-2569).—The *butylxylidine* [ $Me_2 : C_4H_9 : NH_2 = 1 : 3 : 5 : 2$ ] obtained by reducing solid nitrobutylxylene (m. p.  $85^\circ$ , *Abstr.*, 1891, 1464) with iron and dilute acetic acid, crystallises from light petroleum in large, rhombic plates, melts at  $32^\circ$ , boils at  $256^\circ$ , and has a faint odour of *m*-cresol; the *hydrochloride* and *sulphate* are somewhat sparingly soluble in cold water. The base does not combine with diazo-compounds, but easily yields a *benzylidene* derivative,  $C_{12}H_{13}N$ , and an *acetyl* derivative which crystallises from dilute alcohol in large plates and melts at  $81^\circ$ ; the *benzoyl* derivative separates from alcohol in slender needles and melts at  $233^\circ$ . On nitration with a mixture of sulphuric acid and 100 per cent. nitric acid, butylxylidine or its acetyl derivative yields a *nitrobutylxylidine* [ $Me_2 : C_4H_9 : NH_2 : NO_2 = 1 : 3 : 5 : 2 : 4$ ], which crystallises from alcohol in long, sulphur-yellow needles and melts at  $89^\circ$ ; using an excess of nitric acid, the same dinitrobutylxylidine



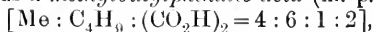
(m. p.  $186^\circ$ ) is obtained as is formed by the reduction of trinitrobutylxylene with alcoholic ammonium sulphide (German Patent, 90291; the melting point here given is  $170^\circ$ ). On similarly nitrating butylacetoxylidide with an excess of nitric acid, *dinitrobutylacetoxylidide* is obtained; it crystallises from alcohol in leaflets and melts at  $192^\circ$ . Dinitrobutylxylidine (m. p.  $186^\circ$ ) can only be acetylated with acetic anhydride, when it yields a *diacetyl* derivative,  $C_{16}H_{21}O_6N_2$ , separating from alcohol in granular crystals, and melting at  $154^\circ$ . The *formyl* derivative of butylxylidine crystallises from alcohol in long, silky needles, and melts at  $173^\circ$ ; the *thiocarbamide* derived from the base separates from alcohol in small needles and melts at  $234^\circ$ , whilst the corresponding *thiocarbimide* separates in thick needles, and melts at  $83^\circ$ .

Attempts to oxidise butylacetylaldehyde to a carboxylic acid with neutral aqueous potassium permanganate failed, but the nitrobutylxylene, melting at  $85^{\circ}$ , gave, on oxidation in alkaline solution, a *nitrobutylisophthalic acid*  $[(\text{CO}_2\text{H})_2 : \text{C}_4\text{H}_9 : \text{NO}_2 = 1 : 3 : 5 : 2]$ , separating from alcohol in needles and melting above  $300^{\circ}$ ; with 20 per cent. nitric acid, however, a *dinitrobutyltoluic acid* melting at  $219^{\circ}$  is obtained.

On nitrating solid nitrobutylxylene, a *dinitrobutylxylene*,  $[\text{Me}_2 : \text{C}_4\text{H}_9 : (\text{NO}_2)_2 = 1 : 3 : 5 : 2 : 4]$ , is obtained which crystallises from alcohol in yellow needles and melts at  $68^{\circ}$ ; the same compound is obtained on nitrating the liquid *nitrobutylxylene*  $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{NO}_2 = 1 : 3 : 5 : 4]$  (A. Meyer, *Dis. Basel*, 1894), which boils at  $258^{\circ}$  under 746 mm., at  $158^{\circ}$  under 30 mm. pressure, and has a sp. gr. 1.042 at  $21^{\circ}$ . A second *dinitrobutylxylene*  $[\text{Me}_2 : \text{C}_4\text{H}_9 : (\text{NO}_2)_2 = 1 : 3 : 5 : 4 : 6]$  is obtained by eliminating the amino-group, by means of the diazo-reaction, from the dinitrobutylxylidine melting at  $186^{\circ}$ ; it crystallises from alcohol in stout, slightly yellow needles, from light petroleum in rhombic plates, and melts at  $84^{\circ}$ . On reducing the dinitrobutylxylene melting at  $68^{\circ}$  with alcoholic ammonium sulphide, the above-described nitrobutylxylidine (m. p.  $89^{\circ}$ ) is obtained; the latter, again, on nitration, yields dinitrobutylxylidine (m. p.  $186^{\circ}$ ) and, on elimination of the amino-group by the diazo-reaction, the foregoing liquid nitrobutylxylene. On these facts, the structural formulæ attributed to all the foregoing compounds are based. On reduction, the liquid nitrobutylxylene gives a *butylxylidine*  $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{NH}_2 = 1 : 3 : 5 : 4]$ , which boils at  $246^{\circ}$ , and yields a *benzoyl* derivative,  $\text{C}_{19}\text{H}_{23}\text{ON}$ , melting at  $206^{\circ}$ ; the *hydrochloride* and *sulphate* are sparingly soluble in water.

Butylxyl cyanide (m. p.  $88^{\circ}$ ) prepared from butylxylidine (m. p.  $32^{\circ}$ ), has, from the foregoing facts, the structure  $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{CN} = 1 : 3 : 5 : 2]$ , and the structure of its dinitro-derivative (m. p.  $110^{\circ}$ , "cyanide musk," German Patent, 84336) is determined, as well as that of dinitrobutylxylazimide ("azimide musk," German Patent, 99256).

Since butylxylaldehyde (*Ber.*, 1898, 31, 2647) on treatment with acetic anhydride yields a *butylxyl cyanide* which crystallises from light petroleum in white needles, melts at  $70^{\circ}$ , and is different from that melting at  $88^{\circ}$ , obtainable from butylxylidine (m. p.  $32^{\circ}$ ), it follows that the structure of butylxylaldehyde is  $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{CHO} = 1 : 3 : 5 : 4]$ . That butylxyl methyl ketone has an analogous structure is shown by the fact that the derived butylxylglyoxylic acid (*Abstr.*, 1898, i, 524), on oxidation with manganese dioxide in sulphuric acid solution, yields a *methylbutylphthalic acid* (m. p.  $173^{\circ}$ )



which on heating above its melting point loses carbon dioxide and gives rise to a *butyltoluic acid* which crystallises from alcohol in white leaflets, melts at  $167^{\circ}$ , and, being different from the three known methylbutylbenzoic acids (*Effront*, *Abstr.*, 1885, 151; *Baur-Thurgau*, *Abstr.*, 1898, i, 524) has necessarily the structure  $[\text{CH}_3 : \text{C}_4\text{H}_9 : \text{CO}_2\text{H} = 1 : 5 : 4]$ . The ease with which the carboxyl group in position 3 in methylbutylphthalic acid is displaced on heating is noteworthy, seeing

that the same group in butyltoluic acid [ $\text{CH}_3 : \text{C}_4\text{H}_9 : \text{CO}_2\text{H} = 1 : 5 : 3$ ] is only removed by strongly heating with lime.

Since the methyl ketone prepared from *m*-butyltoluene (*loc. cit.*), yields on oxidation with dilute nitric acid Effront's 2-methyl-4-butylbenzoic acid (m. p.  $140^\circ$ ), and on further oxidation with potassium permanganate a butylphthalic acid, it is evident that the ketone residue occupies position 4.

W. A. D.

**Action of Iodine and Mercuric Oxide on Styrene and Saffrole.** By J. BOUGAULT (*Compt. rend.*, 1900, 131, 528—530).—When styrene is treated with iodine and yellow mercuric oxide in presence of alcohol, it yields a highly refractive oily liquid which cannot be distilled without decomposing, and probably has the constitution  $\text{CHPhI} \cdot \text{CH}_2 \cdot \text{OH}$ ; when treated with silver nitrate, it yields phenylacetaldehyde. When saffrole is treated in the same way, the product of the reaction does not yield an aldehyde on treatment with silver nitrate. It would seem (this vol., i, 472) that all the iodohydrins of the glycols of the general formula  $\text{R} \cdot \text{CHI} \cdot \text{CH}_2 \cdot \text{OH}$  yield an aldehyde on elimination of hydrogen iodide, and the fact that saffrole behaves differently indicates that the generally accepted constitution of this substance is incorrect.

C. H. B.

**Double Salts of Bismuth Chloride with some Organic Bases.** By O. HAUSER and LUDWIG VANINO (*Ber.*, 1900, 33, 2271—2272).—*Bismuth aniline chloride*,  $\text{BiCl}_3 \cdot 3(\text{NH}_2\text{Ph}, \text{HCl})$ , obtained by dissolving the calculated quantities of bismuth oxide and aniline hydrochloride in alcoholic hydrogen chloride, crystallises in colourless needles, which gradually darken. Similar compounds are formed by *o*- and *p*-toluidine;  $\alpha$ - and  $\beta$ -naphthylamine, however, do not yield double salts with bismuth chloride.

If solutions of bismuth oxide and pyridine in alcoholic hydrogen chloride are mixed, a voluminous white precipitate of the *double salt*,  $\text{BiCl}_3 \cdot 2(\text{C}_5\text{H}_5\text{N}, \text{HCl})$ , is produced, which is at first amorphous but gradually becomes crystalline. Quinoline behaves in a similar manner, yielding the *double salt*,  $\text{BiCl}_3 \cdot 2(\text{C}_9\text{H}_7\text{N}, \text{HCl})$ . Both these salts sublime with very little decomposition.

E. G.

**New Synthesis of Secondary Amines.** By ALFRED TINGLE (*Amer. Chem. J.*, 1900, 24, 276—281).—When ethyl salicylate (1 mol.) and aniline (3 mols.) are heated together for 7 hours, the reaction is very incomplete, and most of the ester can be recovered unchanged; small quantities of salicylaniline, phenol, and a base which is probably ethylaniline, are obtained. Under similar conditions *iso*amyl salicylate and aniline react to about the same extent; phenol is produced, together with a small quantity of a base, which appears to be *iso*-amylaniline.

By the action of dry ammonia on boiling methyl salicylate, dimethylamine and other products are formed.

E. G.

**Action of Cyanogen Bromide on Tertiary Amines.** II. By JULIUS VON BRAUN (*Ber.*, 1900, 33, 2728—2734; 2965. Compare this vol., i, 430).—The tertiary aromatic amines containing *isopropyl* and allyl radicles react more vigorously with cyanogen bromide than the corre-

spouding propyl and ethyl bases, the reactivity of the *isopropyl* and allyl groups being intermediate between that of methyl and ethyl. The allyl group is most readily detached from the aminic nitrogen whilst the *isopropyl* radicle is retained most tenaciously; in the following series, allyl, methyl, ethyl, propyl, and *isopropyl*, the radicles are arranged in ascending order of their affinity for nitrogen.

*Diisopropylaniline*, when treated with cyanogen bromide, yields *diisopropylaniline hydrobromide* and *phenylisopropylcyanamide*, an oil boiling at 136—139° under 10 mm. and at 275° under atmospheric pressure. The former compound is produced by the action of *isopropyl* bromide on *diisopropylaniline* at 150° but not from *isopropyl* bromide and *isopropylaniline*.

*Propylisopropylaniline*, prepared either from *propylaniline* and *isopropyl* iodide or from *isopropylaniline* and *propyl* iodide, is a yellow liquid boiling at 216—217°. When treated with cyanogen bromide it yields *phenylisopropylcyanamide* and a deliquescent product which, in all probability, is the hydrochloride of the unaltered base.

*Ethylisopropylaniline*, obtained from *isopropyl* iodide and *ethylaniline*, is a colourless liquid boiling at 214—215°; it yields two compounds with platinic chloride, a normal *platinichloride* melting at 199°, and another substance containing less platinum which melts at 159—160°; the latter may be a substituted platinum base. *Ethylisopropylaniline* reacts less vigorously with cyanogen bromide than the amines previously described, the products of reaction are ethyl bromide and *phenylisopropylcyanamide*.

*Methylisopropylaniline* results from the action of methyl iodide on *isopropylaniline*; it is a colourless oil boiling at 212—213°; the *platinichloride* melts at 196—197°. The base reacts more vigorously with cyanogen bromide than the preceding amine, the products are methyl bromide, *phenylisopropylcyanamide* and a deliquescent salt which could not be analysed.

*Methylallylaniline*, obtained either from methyl iodide and *allylaniline*, or from allyl iodide and *methylaniline*, is a yellow liquid boiling at 214—216°; it reacts very energetically with cyanogen bromide, yielding allyl bromide, *phenylmethylecyanamide*, and an oily substance containing bromine (compare Wedekind, Abstr., 1899, i, 353, 636).

*Ethylallylaniline*, readily prepared from allyl iodide and *ethylaniline*, reacts quite as readily with cyanogen bromide, giving rise to allyl bromide, *phenylethylecyanamide* and an oil containing bromine.

*Dipropylallylamine* and the cyanogen compound yield allyl bromide and *dipropylecyanamide*.

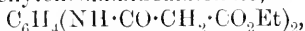
*isoPropylallylaniline*, prepared from *isopropylaniline* and allyl iodide, is a colourless oil which slowly darkens; it boils at 223—227°; with cyanogen bromide, it furnishes *phenylisopropylcyanamide* and *isopropylallylaniline hydrobromide*.  
G. T. M.

**Preparation of Phenylated Guanidines from Diphenylcyanamide.** By JULIUS VON BRAUN (*Ber.*, 1900, 33, 2724—2725. Compare this vol., i, 430).—Tetraphenylguanidine is obtained by heating diphenylcyanamide and diphenylamine at 170—180°, its hydrochloride being produced when diphenylamine hydrochloride is employed.  $\beta$ -Tri-



phenylguanidine is produced in a similar manner either from cyananiline and diphenylamine hydrochloride or from diphenyleyanamide and aniline, the yield in the latter case being very poor. A yellow, soluble *compound* melting at  $52^{\circ}$  is obtained by heating together ammonia and diphenyleyanamide at high temperatures; this substance is possibly a biguanide. G. T. M.

**Formation and Stability of Acid Amides.** By RICHARD E. MEYER and G. VON LUTZAU (*Chem. Centr.*, 1900, ii, 562—563; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1899, 86—88).—The carbamides of the meta- and para-series containing closed carbon chains are less stable than those of the ortho-series; thus whilst the former are easily decomposed by heating with fuming hydrochloric acid at  $160^{\circ}$ , or with alcoholic ammonia at  $120^{\circ}$ , the latter are not attacked under these conditions. By the action of *p*-phenylenediamine on ethyl malonate, ethyl *p*-phenylenediaminomalonate,



is formed and under certain conditions small quantities of malonamide are also obtained. By the action of *p*-phenylenediamine on ethyl succinate, however, *p*-phenylsuccinimide,  $\text{C}_6\text{H}_4\begin{matrix} \text{NH}\cdot\text{CO}\cdot\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CO}\cdot\text{CH}_2 \end{matrix}$ , is formed, the greater length of the succinic acid chain facilitating the formation of a closed chain, although according to Hjelt (*Abstr.*, 1898, ii, 566) oxalates should show the greatest tendency to form closed chains. E. W. W.

**Anilines and Anilides.** By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1900, 33, 2396—2400).—*o*-Chloroformanilide,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CHO}$ , crystallises from light petroleum in plates and melts at  $77^{\circ}$ . *o*-Chlorobenzanilide,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NHBz}$ , crystallises from alcohol in dilute needles and melts at  $99^{\circ}$ . *o*-Bromoformanilide melts at  $87^{\circ}$ . 3:5-Dibromoformanilide crystallises from alcohol in long needles and melts at  $100^{\circ}$ ; 3:5-dibromoacetanilide crystallises from alcohol in long needles and melts at  $231^{\circ}$ ; 3:5-dibromobenzanilide crystallises in short, stout prisms and melts at  $169^{\circ}$ . 4-Chloro-2-bromoaniline crystallises from light petroleum in silky needles, melts at  $69^{\circ}$ , and boils at  $127^{\circ}$  under 20 mm. pressure; 4-chloro-2-bromoacetanilide, formed by isomeric change from acetyl bromoamino-4-chlorobenzene, crystallises from alcohol in rhombic forms and melts at  $137^{\circ}$ ; 4-bromo-2-chloroacetanilide, prepared in a similar way from acetylchloroamino-4-bromobenzene, melts at  $151^{\circ}$ , and is hydrolysed to Fittig and Büchner's 2-chloro-4-bromoaniline (*Abstr.*, 1878, 50), which melts at  $73^{\circ}$ . 2-Bromo-4-nitroacetanilide crystallises from a mixture of benzene and light petroleum in yellow, four-sided prisms and melts at  $129^{\circ}$ . 2:6-Dibromo-4-nitroacetanilide crystallises in pale yellowish, transparent prisms and melts at  $234^{\circ}$ ; Nölting, Grandmougin and Michel's compound, melting at  $135^{\circ}$  (*Ber.*, 1892, 25, 333), is the diacetyl and not the monoacetyl derivative. 2:6-Dichloro-4-nitroacetanilide crystallises from cold alcohol in long, silky needles and melts at  $140^{\circ}$ . 4-Bromo-1-formonaphthalide,  $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}\cdot\text{CHO}$ , crystallises from chloroform in minute, white needles and melts at  $172^{\circ}$ .

T. M. L.

**Conversion of  $\alpha$ -Amino-acids into Phenylhydantoins.** By ANTOINE MOUNEYRAT (*Ber.*, 1900, **33**, 2393—2396).—The hydantoic acids prepared by the action of phenylcarbimide on  $\alpha$ -amino-acids (Paal, *Abstr.*, 1894, i, 332) can be converted into hydantoins by heating with dilute hydrochloric acid. In this way,  $\gamma$ -phenylhydantoin (Guareschi, *Abstr.*, 1892, 828) has been prepared from aminoacetic acid, and Küln's phenylmethylhydantoic acid was converted into

phenylmethylhydantoin, 
$$\begin{array}{c} \text{CHMe}\cdot\text{CO} \\ | \\ \text{NH}\text{---}\text{CO} \end{array} \text{>NPh},$$
 which crystallises from dilute alcohol in needles and melts at 172—173°. Phenylethylhydantoic acid, prepared by the action of phenylcarbimide on  $\alpha$ -aminobutyric acid, melts with liberation of gas at 170° (corr.); the hydantoin melts and decomposes at 126—127° (corr.). Phenylisobutylhydantoin, 
$$\begin{array}{c} \text{C}_4\text{H}_9\beta\cdot\text{CH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{array} \text{>NPh},$$
 and phenylbenzylhydantoin,



were prepared from the hydantoic acids (Fischer, this vol., 646); the latter hydantoin crystallises in needles and melts at 173—174°.

T. M. L.

**Convenient Method for the Preparation of Aromatic Thiocarbamides.** By JULIUS VON BRAUN (*Ber.*, 1900, **33**, 2726—2727).—Substituted thiocarbamides readily result from the action of various oxidising agents on aromatic dithiocarbamates, or mixtures of carbon disulphide and aromatic amines. A mixture of carbon disulphide (1 mol.) and aromatic amine (2 mols.) is shaken up with 3 per cent. hydrogen peroxide and the product extracted with alcohol; the carbamide is obtained from the solution in practically quantitative yield. The method is not applicable to the aliphatic amines.

G. T. M.

**Action of Sodium Ethoxide on Ethyl Anilinoacetate.** By DANIEL VORLÄNDER and A. T. DE MOULPIED (*Ber.*, 1900, **33**, 2467—2470).—When ethyl anilinoacetate is boiled for a short time with alcoholic sodium ethoxide, the anhydride of anilinoacetic acid, 
$$\text{NPh} \begin{array}{c} \text{CH}_2\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{CH}_2 \end{array} \text{>NPh},$$
 is formed; it is neutral in character.

When ethyl anilinoacetate is heated with dry sodium ethoxide, with or without anhydrous ether or benzene, a product is obtained which melts and decomposes at 190°, dissolves in alkalis, and apparently has the constitution, 
$$\text{NPh} \begin{array}{c} \text{CH}_2\cdot\text{C}\cdot\text{OH} \\ | \quad | \\ \text{CO}\text{---}\text{C}\cdot\text{NHPh} \end{array}.$$
 With phenylhydrazine (2 mols.) it yields an orange-red, crystalline substance melting at 224°; it forms a *monobenzoyl* derivative melting at 168°. It contains no ethoxyl group, for it can be prepared also from methyl anilinoacetate and sodium methoxide; the product in this case is found not to contain methoxyl when examined by Zeisel's method.

C. F. B.

**Chlorination of Aceto-*m*-toluidide.** By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEU (*Ber.*, 1900, **33**, 2503—2504).—A mono-, di-, or

tri-chloro-derivative may be obtained by treating aceto-*m*-toluidide with sodium chlorate and hydrochloric acid in glacial acetic acid, the nature of the product depending on the amount of chlorinating agent employed.

2:4-*Dichloro-5-acetotoluidide* crystallises from alcohol in colourless needles and melts at 156°. 2:4-*Dichloro-5-toluidine*, prepared by hydrolysing the preceding compound, crystallises from light petroleum and melts at 85°; it is volatile in steam. The *trichloroacetotoluidide* melts at 181°.

G. T. M.

**Constitution of Metapurpuric Acid.** By WALTHER BORSCHKE (*Ber.*, 1900, 33, 2718—2723).—Potassium metapurpurate, when prepared by mixing 2:4-dinitrophenol with potassium cyanide in aqueous or alcoholic solution, has a composition agreeing best with the formula  $C_7H_2O_4N_3K \cdot 2H_2O$ . This salt decomposes on treatment with cold dilute sulphuric acid into nitrous oxide, tarry products, and a small amount of 2:4-dinitrohydroxybenzonitrile; it explodes when heated or when moistened with concentrated sulphuric acid.

2:4-Dinitrohydroxybenzonitrile is readily prepared by oxidising potassium metapurpurate with dilute nitric acid; it crystallises very readily in pale yellow, lustrous, flattened needles and melts at 125—126°.

With a view of detecting the presence of the group (NH·OH) in purpuric acid, the potassium salt was treated with sodium nitrite and dilute acetic acid; the nitrous acid, however, behaves as an oxidising agent, and the *potassium* salt of 2:4-dinitrohydroxybenzonitrile is produced; this substance crystallises with  $2H_2O$  in yellow needles, and decomposes explosively on heating.

G. T. M.

**Purification of Phloroglucinol.** By G. S. FRAPS (*Amer. Chem. J.*, 1900, 24, 270—271).—In order to prepare a solution of phloroglucinol sufficiently free from diresorcinol for the estimation of pentosans in vegetable materials, the following method is adopted. Commercial phloroglucinol is extracted with hot hydrochloric acid of sp. gr. 1·06; the hot solution is poured into a larger quantity of hydrochloric acid of the same strength, left for several days, and then filtered; by this means, the greater part of the diresorcinol is removed.

E. G.

**Occurrence of Phenylethyl Alcohol in Rose Blossoms.** By HEINRICH WALBAUM (*Ber.*, 1900, 33, 2299—2302. Compare this vol., i, 509).—Dried rose leaves, when extracted with ether, and fresh rose leaves, when extracted with light petroleum, yield phenylethyl alcohol.

R. H. P.

**Compounds of Magenta with Acid Colouring Matters having a Basic Chromophore.** By ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1900, [iii], 23, 771—784. Compare this vol., i, 356, 522, and 614).—The compounds of magenta with the sulphonated azo-colouring matters, described in the first part of this paper, have already been noticed (this vol., i, 614).

Alkali blue, acid violet 4BN, acid violet 6B, and sulphonmagenta

combine with as many mols. of magenta as they contain sulphonie groups, namely, 1, 2, 3, and 4 mols. respectively.

Gallanilic indigo PS, gallanilic green, and rosinduline A all contain one sulphonie group and combine with 1 mol. of magenta, whilst azocarmine A, which contains two sulphonie groups, combines with 2 mols. of magenta. Oxynaphthine contains a hydroxyl and a carboxyl group but no sulphonie group; it combines with 1 mol. of magenta.

Thioflavine S and primuline contain one sulphonie group and combine with 1 mol. of magenta whilst thiazole yellow and erika B contain two sulphonie groups and combine with 2 mols. of magenta.

The results described in this and preceding papers are thus summarised. Among acidic colouring matters having an acid chromophore reinforced or attenuated by the substitution of acid or basic groups, the nitro-colours and colours derived from quinoneoximes, hydroxyketones, and hydroxyquinones combine with 1 mol. of magenta, whatever may be the number of substituting nitro- or hydroxyl groups. In the nitro-derivatives, the presence of sulphonie groups increases the affinity for magenta, whilst with the oxyquinone derivatives the reverse is the case. Derivatives of triphenylmethane of the type of rosolic acid containing only substituted hydroxyl groups combine with 1 mol. of magenta, but if carboxyl groups are also present, the number of mols. of magenta affixed is correspondingly increased. Colouring matters of the phthalein series combine with 2 mols. of magenta. Acidic colouring matters having a basic chromophore rendered acid by the substitution of acid groups, such as sulphonated azo-colours, sulphonated derivatives of triphenylmethane, sulphonie and carboxyl derivatives of quinoneimide, and sulphonated thiazole and azothiazole derivatives combine with as many mols. of magenta as they contain sulphonie groups. In the case, however, of sulphonated azo-colouring matters containing hydroxyl groups in a nucleus other than that containing the sulphonie groups, an additional mol. of magenta is affixed if a sufficient quantity of alkali to react with the hydroxyl groups is added. This result is, perhaps, to be explained by a molecular transformation, as suggested by Farmer and Hantzsch (this vol., i. 122).

N. L.

**Resolution of Racemic Amino-acids into Optically Active Components. III.** By EMIL FISCHER (*Ber.*, 1900, 33, 2370—2382. Compare this vol., i, 172).—Benzoyl-*D*-leucine, which is levorotatory in alkaline solution, may be obtained from the racemic compound by means of the cinchonine salt, and the dextrorotatory isomeride can be isolated in the form of quinidine salt.

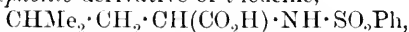
*Benzoyl-L-leucine* crystallises in colourless, rhombic plates on adding petroleum to the solution in ether, and melts at 137—141° (corr.); it dissolves in 200 parts of boiling water, from which it crystallises in slender needles.

*Benzoyl-D-leucine*, obtained on resolving the foregoing substance into its active components by means of the cinchonine salt, crystallises in short prisms containing  $\frac{1}{2}$  mol. of ether of crystallisation, which is removed at 50°; when containing ether, it melts indefinitely at about

60°, but when free from ether fuses at 105—107° (corr.). It dissolves in 120 parts of boiling water, from which it crystallises in short prisms; an 8.46 per cent. solution in sodium hydroxide (1 mol.) at 20° gives  $[\alpha]_D - 6.39^\circ$ . The *cinchonine* salt crystallises in aggregates of needles melting at 85°. The *d*-leucine, obtained by hydrolysing the benzoyl derivative with 10 per cent. hydrochloric acid, gave  $[\alpha]_D - 16.91^\circ$  in a 4.73 per cent. hydrochloric acid solution at 20°.

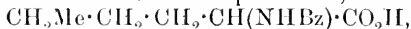
*Benzoyl-l-leucine*, isolated in the form of quinidine salt, forms crystals containing ether which melt first at 60°, afterwards at 105—107°;  $[\alpha]_D$  is +6.59° at 20°. The *quinidine* salt forms colourless prisms and rectangular plates. The *l*-leucine obtained on hydrolysis gave  $[\alpha]_D + 15.59^\circ$ .

The *benzenesulphonic* derivative of *i*-leucine,



crystallises in prisms which sinter at 140°, and begin to melt at 146° (corr.); the alkali salts are readily soluble in water, and crystallise in needles, whilst the *lead* and *silver* salts, which are also crystalline, dissolve more sparingly. The phenylcarbimide compound of *r*-leucine,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from dilute alcohol in colourless needles, melting and evolving gas at 165° (corr.); it dissolves in about 300 parts of boiling water and in 2 parts of boiling alcohol. The *silver* salt crystallises in small needles.

The *benzoyl* derivative of  $\alpha$ -aminocaproic acid,



crystallises in six-sided leaflets and melts at 134° (corr.); the *barium* salt crystallises in small prisms and the *silver* salt in leaflets. The *benzenesulphonic* derivative,  $\text{C}_{12}\text{H}_{17}\text{O}_4\text{NS}$ , crystallises in aggregates of thin prisms and melts at 125° (corr.).

M. O. F.

**Resolution of Racemic Amino-acids into Optically Active Components. IV.** By EMIL FISCHER and ANTOINE MOUNEYRAT (*Ber.*, 1900, 33, 2383—2393. Compare foregoing abstract).—*Benzoyl-d-phenylalanine*, prepared by resolving the racemic compound into its components with cinchonine, crystallises from 200 parts of boiling water in colourless needles melting at 145—146° (corr.); the alkaline solution has  $[\alpha]_D - 17.1^\circ$  at 20°. The *cinchonine* salt crystallises from 100 parts of hot water in colourless needles, and melts at 180—181°. *d*-Phenylalanine crystallises from water in leaflets, and melts, evolving gas, at 283—284° (corr.); a 2 per cent. solution in water has  $[\alpha]_D + 35.08^\circ$  at 16°, and a 3.5 per cent. solution in 18 per cent. hydrochloric acid has  $[\alpha]_D + 7.07^\circ$ . The *phenylcarbimide* compound,  $\text{CH}_2\text{Ph} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from 300 parts of boiling water in colourless needles melting at 180—181° (corr.); the alkaline solution has  $[\alpha]_D + 61.27^\circ$  at 20°. *Benzoyl-l-phenylalanine* has not yet been obtained free from the levorotatory isomeride.

*r*-Benzoyl- $\alpha$ -aminobutyric acid,  $\text{CH}_2\text{Me} \cdot \text{CH}(\text{NH} \cdot \text{Bz}) \cdot \text{CO}_2\text{H}$ , crystallises from 25 parts of boiling water, sinters at 140°, and melts at 145—146° (corr.). *r*-*Benzenesulphaminobutyric acid* melts at 148—149° (corr.), and resembles the benzoyl derivative in solubility. *d*-Benzoyl- $\alpha$ -aminobutyric acid crystallises from water and melts at 120—121°.

(corr.); the solution in sodium hydroxide (1 mol.) has  $[\alpha]_D + 30.8^\circ$  at  $20^\circ$ . The *morphine* salt melts at  $145\text{--}146^\circ$ . *d*- $\alpha$ -Aminobutyric acid forms colourless leaflets which melt and decompose at  $303^\circ$  (corr.); a 5.4 per cent. aqueous solution has  $[\alpha]_D + 8.0^\circ$ . The *hydrochloride* crystallises in needles, and has  $[\alpha]_D + 14.51^\circ$  in a 5 per cent. aqueous solution. *l*-Benzoyl- $\alpha$ -aminobutyric acid has  $[\alpha]_D - 31.8^\circ$ , and in every other respect corresponds with the dextrorotatory compound; the *brucine* salt forms large, transparent crystals which melt at  $86\text{--}87^\circ$ . *l*- $\alpha$ -Aminobutyric acid has  $[\alpha]_D - 7.92^\circ$ ; the *hydrochloride* has  $[\alpha]_D - 14.34^\circ$ .

M. O. F.

**Polymerisation of *p*-Toluonitrile.** By JAN PIEPES-PORATYŃSKI (*Chem. Centr.*, 1900, ii, 477; from *Bull. Acad. Sci. Cracow*, 1900).—*p*-Cyanotoline,  $(C_6H_4MeCN)_3$ , prepared by heating *p*-toluonitrile, *p*-toluic chloride, ammonium chloride, and aluminium chloride at  $150^\circ$  for a long time, crystallises from benzene in white, lustrous, needle-shaped crystals, melts at  $276\text{--}277^\circ$ , and is insoluble in water, very soluble in hot benzene, and slightly so in alcohol. *p*-Toluline or tri-*p*-tolylglyoxaline,  $C_{24}H_{22}N_3$ , obtained by the action of zinc dust and boiling glacial acetic acid on *p*-cyanotoline, melts at  $234\text{--}235^\circ$ , is insoluble in water, and forms a *hydrochloride* and a *platinichloride*; in presence of alcoholic potash, it is oxidised by exposure to air, forming a strongly fluorescent solution. One hundred parts of alcohol at  $16^\circ$  dissolve 2.82 of toluline and on boiling 9.851 parts.

E. W. W.

**Boiling and Subliming Points of some Allo-acids.** By CARL LIEBERMANN and C. N. RIIBER (*Ber.*, 1900, 33, 2400—2402).—Cinnamic, cinnamylideneacetic, and furfurylacrylic acids, and the corresponding allo-acids, can be distilled or sublimed unchanged in a cathode vacuum; *allocinnamylideneacetic acid* is partially decomposed with loss of carbon dioxide when impure. The following table of temperatures is given:

Cinnamic acid, sublimation point .....	108°
<i>allo</i> Cinnamic acid, boiling point .....	95
Cinnamylideneacetic acid, sublimation point.....	145
<i>allo</i> Cinnamylideneacetic acid, sublimation point .....	130
Furfurylacrylic acid, sublimation point.....	112
<i>allo</i> Furfurylacrylic acid, sublimation point... ..	95

T. M. L.

**Bromocoumarins and their Derivatives. III.** By HUGO SIMONIS and G. WENZEL (*Ber.*, 1900, 33, 2326—2328. Compare this vol., i, 496).—3:6:8-Tribromocoumarin can be synthesised by treating 6:8-dibromocoumarin dibromide (from 3:5-dibromosalicylaldehyde and acetic anhydride) with cold alcoholic potash. 6-Bromocoumarin dibromide, obtained by the action of bromine on 6-bromocoumarin, is an unstable compound which crystallises in thick prisms, melts at  $102\text{--}105^\circ$ ; when treated with alcoholic potash in the cold, it yields 3:6-dibromocoumarin, and when warmed bromocoumarilic acid.

The paper contains a tabular statement of the known bromo-derivatives of coumarin, coumarone, and coumarilic acid.

R. H. P.

**Action of Phenylhydrazine and of Hydroxylamine on Ethyl Phenylcyanopyruvate.** By EMIL ERLÉNMEYER, jun. (*Ber.*, 1900, 33, 2592—2595).—When ethyl  $\beta$ -cyanophenylpyruvate is treated with phenylhydrazine acetate, the *hydrazone* is formed in two isomeric modifications; one crystallises in yellow prisms melting at 107—108°, and the other in fascicular groups of needles melting at 112—113°. The cause of the isomerism of these two forms has not yet been ascertained. When the ester is treated with pure phenylhydrazine, only a small amount of the hydrazone is produced, the greater part of the ester being converted into benzyl cyanide and monoethyl oxalate monophenylhydrazide, a portion of which is then converted into oxalyldiphenylhydrazine.

The *oxime* of ethyl  $\beta$ -cyanophenylpyruvate forms large crystals melting at 119—120°, and has an acid reaction. No separation into optically active components could be effected by means of the cinchonine salt.

A. H.

**Formation of Indigotin from Ethyl Anthranilate.** By DANIEL VORLÄNDER and C. KOETTNITZ (*Ber.*, 1900, 33, 2466—2467. Compare Henze, this vol., i, 119).—*Ethyl anthranilic acid malonate* (*carboxyphenyliminomalonate*),  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , is obtained by boiling anthranilic acid with ethyl bromomalonate and water; it melts at 127°, and gives a reddish-brown coloration with ferric chloride. The corresponding *acid* can be obtained from it by hydrolysis, and the *triethyl ester* by condensing ethyl anthranilate with ethyl bromomalonate; these melt at 185° and 122—124° respectively. All yield indigotindisulphonic acid when heated with a large quantity of concentrated sulphuric acid, or indigotin when fused with caustic potash, the triethyl ester, however, reacting less readily than the other compounds.

C. F. B.

**Formation of Indigotin from Woad.** By MARTINUS W. BEIJERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 101—116).—The view formerly expressed that woad contains free indoxyl is now found to be incorrect (this vol., i, 230, 403); this substance is really present in an unstable compound called *isatan*, and is set free by the action of an enzyme, *isatase*. On extracting woad leaves with dilute acid, a solution is obtained which remains unchanged in the air, although indoxyl dissolved in acid of the same strength is oxidised to indigotin; the difference is due to the fact that the acid extract of the plant contains *isatan*, which is stable under these conditions. A solution containing 2—3 per cent. of oxalic acid may be employed in extracting *isatan* from woad leaves; in more dilute acid, the *isatase* becomes active, whereas stronger acid decomposes the substance, yielding indoxyl and brown decomposition products. Dilute solutions of other acids and of acid salts may also be employed in the extraction.

Indican is not affected by alkalis, whereas *isatan* is decomposed even in dilute alkaline solutions and by feebly alkaline salts, such as

disodium hydrogen phosphate or ammonium carbonate. Both indican and isatan are decomposed by acids, the latter also by boiling with acid salts.

Isatase is found in the residue obtained by extracting the disintegrated plant first with alcohol and afterwards with water. Whereas isatan is restricted to the growing parts, isatase is found throughout the plant, and its distribution in the cell is similar to that of the indigo enzymes.

Isatase acts on isatan only in neutral or feebly acid solution, the optimum temperature of reaction being 48—50°; at 70°, the enzyme is completely destroyed. It does not act on indican; isatan, on the other hand, is not decomposed by indigo enzymes and ordinary bacteria.

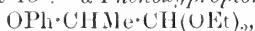
Indoxyl is readily produced from woad by extracting the young leaves with a 0.5 per cent. solution of disodium hydrogen phosphate.

G. T. M.

**Synthesis and Degradation in the Coumarone Series.** By RICHARD STORMER (*Annalen*, 1900, 312, 237—336; 313, 79—97. Compare Abstr., 1895, i, 464; 1897, i, 526).—The introductory portion of the paper deals with comparatively recent syntheses in the coumarone series, including the condensation of aryloxyacetals under the influence of zinc chloride dissolved in glacial acetic acid.

In preparing coumarone from phenoxyacetal by the author's method, and likewise when the condensation is effected by means of fused oxalic acid, the yield is greatly reduced by the production of a polymeride. This substance, after several crystallisations from dilute acetic acid, forms a yellowish-brown powder which melts between 80° and 100°, and decomposes at 170—180°; it dissolves very readily in ether, benzene, and chloroform, but is less soluble in alcohol, particularly when hot. Destructive distillation resolves it into phenol, coumarone, and water, in which respect it differs from  $\alpha$ -paracoumarone, which yields only traces of phenol when distilled; moreover, determinations of molecular weight agree more closely with the expression  $(C_8H_6O)_6$  than with  $(C_8H_6O)_4$ , or with  $(C_8H_6O)_3$ , which represent  $\alpha$ - and  $\beta$ -paracoumarone respectively.

[With KISSEL.]—1-Methylcoumarone  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CH \end{smallmatrix} CMe$ , prepared from  $\alpha$ -phenoxypropionacetal, is a colourless liquid having an agreeable odour; it boils at 189—191°, has a sp. gr. 1.0505 at 14°, and the refractive index 1.5495 at 15°.  *$\alpha$ -Phenoxypropionacetal*,



obtained from  $\alpha$ -bromopropacetal, phenol, and sodium ethoxide in an autoclave at 200—210°, boils at 131—132° under 14 mm.;  *$\alpha$ -phenoxypropaldehyde*,  $C_6H_5 \cdot OCHMe \cdot CHO$ , boils at 99—101° under 16 mm. pressure, and yields the *oxime* and *semicarbazone* melting at 110° and 161.5° respectively.

2-Methylcoumarone,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CMe \end{smallmatrix} CH$ , derived from phenoxyacetone (Abstr., 1895, i, 464), has been already described by Hantzsch (Abstr., 1886, 707); it boils at 193—194°, has a sp. gr. 1.0596 at 11°,



and the refractive index  $[n]_D$  1.5535 at 16°. It is fairly stable towards concentrated sulphuric acid, being converted but slowly into a polymeride,  $(C_6H_3O)_4$ ; this differs from the substance which accompanies 2-methylcoumarone when prepared from phenoxyacetone and sulphuric acid, and has the formula  $(C_6H_3O)_6$ .

4-Methylcoumarone, 5-methylcoumarone, and 6-methylcoumarone,  $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CH$ , prepared from the three tolyloxyacetals, have been already described (Störmer, Abstr., 1897, i, 527).

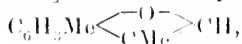
Of the fifteen possible dimethylcoumarones, only the 2:4-dimethylcoumarone of Hantzsch and Lang (Abstr., 1886, 706) has been known hitherto; the authors have increased this number to eleven.

1:4-Dimethylcoumarone,  $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CMe$ , boils at 211–213°, has a sp. gr. 1.0491 at 10°, and refractive index 1.5396 at 15°. *p*-Cresoxypropacetal,  $C_6H_4Me \cdot O \cdot CHMe \cdot CH(OEt)_2$ , boils at 272°, and *p*-cresoxypropaldehyde,  $C_6H_4Me \cdot OCHMe \cdot CHO$ , boils at 109–111° under 13 mm. pressure, and yields an *oxime* and *semicarbazone* which melt at 90–91° and 152° respectively; *p*-cresoxypropionic acid,  $C_6H_4Me \cdot O \cdot CHMe \cdot CO_2H$ , melts at 97°.

1:5-Dimethylcoumarone,  $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CMe$ , prepared from the aldehyde,  $CHO \cdot C_6H_3Me \cdot O \cdot CHMe \cdot CO_2H$ , and alcoholic soda at 190°, is a colourless oil which boils at 217–218°, and forms the *picrate* melting at 58–59°; it has a sp. gr. 1.051 at 12°, and refractive index 1.5541 at 15°. When prepared from *m*-cresoxypropacetal, the coumarone boils at a lower temperature, and yields a *picrate* which melts at 48–49°; this is probably due to admixture with 1:3-dimethylcoumarone. *m*-Cresoxypropacetal boils at 271°, and *m*-cresoxypropaldehyde boils at 119–120° under 18 mm. pressure, and yields an *oxime* and *semicarbazone* which melt at 103° and 161° respectively; *m*-cresoxypropionic acid melts at 105°.

1:6-Dimethylcoumarone,  $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CMe$ , boils at 208–209°, has a sp. gr. 1.0660 at 11°, and refractive index 1.5385 at 15°. *o*-Cresoxypropacetal boils at 139–140° under 15 mm. pressure, and *o*-cresoxypropaldehyde boils at 105–107° under 13 mm. pressure, and yields an *oxime* which melts at 113–114°; *o*-cresoxypropionic acid melts at 93°.

[With HERMES and GROSS.]—2:4-Dimethylcoumarone,



first prepared by Hantzsch and Lang (*loc. cit.*), boils at 218–220° under 747 mm. pressure, and has an intense, persistent odour; it has a sp. gr. 1.0445 at 11°, and refractive index 1.5500 at 16°. The *picrate* melts at 108°. *p*-Cresoxyacetone,  $C_6H_4Me \cdot O \cdot CH_2 \cdot C(OMe)_2$ , boils at 255°, and yields an *oxime*, *phenylhydratone*, and *semicarbazone* melting at 62°, 90°, and 187° respectively.

2:5-Dimethylcoumarone,  $C_6H_3Me \begin{smallmatrix} \diagup O \\ CMe \diagdown \end{smallmatrix} CH$ , a highly refractive

liquid having the odour of peppermint, boils at  $222^{\circ}$ , has a sp. gr. 1.0456 at  $20^{\circ}$  and a refractive index 1.5505 at  $20^{\circ}$ ; the *picrate* melts at  $76^{\circ}$ . *m-Cresoxyacetone* boils at  $248^{\circ}$ , and yields a *semicarbazone* melting at  $147^{\circ}$ ; the *oxime* and *phenylhydrazone* are oils.

2:6-Dimethylcoumarone,  $\text{C}_6\text{H}_3\text{Me}_2\text{C}(\text{O})\text{CH}$ , boils at  $216\text{--}217^{\circ}$  (corr.), and yields a *picrate* which melts at  $68^{\circ}$ . *o-Cresoxyacetone* boils at  $240\text{--}241^{\circ}$ , and yields a *semicarbazone* melting at  $178^{\circ}$ ; the *oxime* and *phenylhydrazone* are oils.

4:6-Dimethylcoumarone, 4:5-dimethylcoumarone, and 3:6-dimethylcoumarone,  $\text{C}_6\text{H}_2\text{Me}_2\text{C}(\text{O})\text{CH}$ , have been already described by the author as *op*-, *mp*-, and *om*-dimethylcoumarones respectively (Abstr., 1897, i, 527); the properties of the corresponding acetals and aldehydes were recorded at the same time.

3:5-Dimethylcoumarone,  $\text{C}_6\text{H}_2\text{Me}_2\text{C}(\text{O})\text{CH}$ , boils at  $219^{\circ}$ , has a sp. gr. 1.037 at  $20^{\circ}$ , and refractive index 1.5485 at  $21^{\circ}$ ; the *picrate* melts at  $61.5^{\circ}$ . *m-Xylenoxyacetal*,

$\text{C}_6\text{H}_3\text{Me}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$  [ $\text{Me}_2:\text{O}=1:3:5$ ], boils at  $287\text{--}288^{\circ}$ ; the *aldehyde hydrate* melts at  $68^{\circ}$ , and yields an *oxime* which melts at  $100.5^{\circ}$ .

[With Boes.]—5:6-Dimethylcoumarone,  $\text{C}_6\text{H}_2\text{Me}_2\text{C}(\text{O})\text{CH}$ , boils at  $218^{\circ}$ , has a sp. gr. 1.038 at  $20^{\circ}$ , and refractive index 1.5478 at  $20^{\circ}$ ; the *picrate* melts at  $63^{\circ}$ . *o-Xylenoxyacetal* (vicinal) boils at  $165^{\circ}$  under 15 mm. pressure; the *aldehyde hydrate* melts at  $75^{\circ}$ , and forms an *oxime* and *semicarbazone* melting at  $106^{\circ}$  and  $184^{\circ}$  respectively.

4-Ethylcoumarone,  $\text{C}_6\text{H}_3\text{Et}\text{C}(\text{O})\text{CH}$ , has been described by Stoermer and Schroeder (Abstr., 1897, i, 527) as *p*-ethylcoumarone; the properties of the corresponding acetal and aldehyde have been also recorded.

6-Ethylcoumarone,  $\text{C}_6\text{H}_3\text{Et}\text{C}(\text{O})\text{CH}$ , boils at  $215^{\circ}$ , has a sp. gr. 1.033 at  $24^{\circ}$ , and refractive index 1.538. *o-Ethylphenoxyacetal*,  $\text{C}_6\text{H}_4\text{Et}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , boils at  $275^{\circ}$ .

2:4:5-Trimethylcoumarone,  $\text{C}_6\text{H}_2\text{Me}_3\text{C}(\text{O})\text{CH}$ , boils at  $249\text{--}250^{\circ}$ , and has a penetrating odour suggesting camphor and peppermint; when cooled artificially, it crystallises in rectangular plates melting at  $40.5^{\circ}$ . The *picrate* melts at  $84\text{--}85^{\circ}$ . *o-Xylenoxyacetone*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{COMe}$  [ $\text{Me}_2:\text{O}=1:2:4$ ], boils at  $272\text{--}273^{\circ}$ ; the *semicarbazone* and *oxime* melt at  $164.5^{\circ}$  and  $70^{\circ}$  respectively.

[With Gross.]—2:3:6-Trimethylcoumarone,  $\text{C}_6\text{H}_2\text{Me}_3\text{C}(\text{O})\text{CH}$ , melts at  $55^{\circ}$ , and boils at  $243^{\circ}$  (corr.); the *picrate* melts at  $98^{\circ}$ . *p-Xylenoxyacetone* [ $\text{Me}_2:\text{O}=1:4:5$ ] boils at  $261^{\circ}$ ; the *semicarbazone* and *oxime* melt at  $182^{\circ}$  and  $132^{\circ}$  respectively.

2 : 4 : 6-*Trimethylcoumarone*,  $\text{C}_6\text{H}_2\text{Me}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CMe} \end{smallmatrix} \text{CH}$ , boils at  $232^\circ$  (corr.), and has a sp. gr.  $1.007$  at  $16^\circ$ ; the picrate melts at  $66^\circ$ . *as-m-Xylenoxyacetone* [ $\text{Me}_2\text{O} = 1 : 3 : 4$ ] boils at  $263^\circ$ ; the *oxime* and *semicarbazone* melt at  $133^\circ$  and  $145^\circ$  respectively.

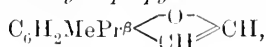
3 : 4 : 6-*Trimethylcoumarone*,  $\text{C}_6\text{HMe}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$ , has been already described as 1 : 3 : 4-trimethylcoumarone (*loc. cit.*).

[With von FINECK.]—*Trimolecular* 3 : 4 : 6-*trimethylcoumarone*,  $(\text{C}_{11}\text{H}_{12}\text{O})_3$ , a bye-product in the condensation of  $\psi$ -cumenoxycetal, crystallises from hot glacial acetic acid in slender, white needles, and melts at  $168^\circ$ ; distillation resolves it into trimethylcoumarone and  $\psi$ -cumenol.

4-*isopropylcoumarone*,  $\text{C}_6\text{H}_3\text{Pr}^\beta \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$ , boils at  $235^\circ$ , has a sp. gr.  $1.055$ , and refractive index  $1.5499$  at  $19.4^\circ$ . *p-isopropylphenoxycetal*,  $\text{C}_6\text{H}_4\text{Pr}^\beta \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$ , boils at  $287-288^\circ$ ; the *aldehyde hydrate* is an oil, and yields a *semicarbazone* and *thiosemicarbazone* melting at  $127-128^\circ$  and  $95^\circ$  respectively.

1 : 3 : 4 : 6-*Tetramethylcoumarone*,  $\text{C}_6\text{HMe}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CMe}$ , solidifies at  $18^\circ$  and boils at  $241-242^\circ$ .  $\psi$ -*Cumenoxypropionycetal*,  $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CH}(\text{OEt})_2$ , boils at  $159-160^\circ$  under 16 mm. pressure.

[With GROSS.]—3 : 6-*Methylisopropylcoumarone*,

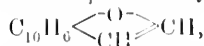


boils at  $241-242^\circ$ , has a sp. gr.  $1.0145$  and refractive index  $1.5363$  at  $16^\circ$ . *Thymoxycetal*,  $\text{C}_6\text{H}_3\text{MePr}^\beta \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$ , boils at  $280-281^\circ$ .

6 : 3-*Methylisopropylcoumarone*,  $\text{C}_6\text{H}_2\text{MePr}^\beta \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$ , boils at  $238-240^\circ$ , has a sp. gr.  $1.0166$ , and refractive index  $1.5291$  at  $17^\circ$ . *Carvacrylacetal* is a colourless oil, and *carvacrylacetaldehyde*,  $\text{C}_6\text{H}_3\text{MePr} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CHO}$ , yields a *semicarbazone* melting at  $255^\circ$ .

4-*tert. Butylcoumarone*,  $\text{CMe}_3 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$ , boils at  $238-241^\circ$ ; in preparing it from butylphenoxycetal, a considerable proportion of butylphenol is regenerated, so that the yield is very small.

[With PAUL SCHRECKENBERGER.]—1-Methyl- $\beta$ -naphthafuran,



melts at  $59^\circ$ , and has been described by Hantzsch (*loc. cit.*); the *picrate* melts at  $156^\circ$ .  $\beta$ -*Naphthoxyacetone*,  $\text{C}_{10}\text{H}_7 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$ , crystallises in lustrous leaflets and melts at  $78^\circ$ ; the *oxime*, *phenylhydrazone*, and *semicarbazone* melt at  $123^\circ$ ,  $154^\circ$ , and  $203^\circ$  respectively. 2-Methyl- $\alpha$ -naphthafuran,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CMe} \end{smallmatrix} \text{CH}$ , has been also described by Hantzsch; it boils at  $296-299^\circ$ .

[With O. RICHTER and K. P. GRALERT.]—1 : 2-*Dibromocoumarone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CBr} \end{smallmatrix} \text{CBr}$ , prepared by the action of bromine on bromo

coumarone in carbon disulphide, melts at  $27^{\circ}$  and boils at  $269-270^{\circ}$ ; further treatment with bromine converts it into *tribromocoumarone*,  $C_8H_3OBr_3$ , which crystallises from alcohol in lustrous needles, melts at  $85^{\circ}$ , and boils at  $315-320^{\circ}$ . Both derivatives are indifferent towards silver oxide, even when heated with it at  $150^{\circ}$  in sealed tubes; concentrated nitric acid converts the dibromide into *dibromonitrocoumarone*,  $C_8H_3O_4NBr_2$ , which crystallises from alcohol in white needles melting at  $188^{\circ}$ .

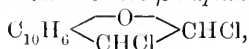
*Trichlorocoumarone*,  $C_8H_3OCl_3$ , obtained when chlorine is passed into an ethereal solution of chlorocoumarone, crystallises from alcohol in long, white needles melting at  $78^{\circ}$  and boils at  $258-260^{\circ}$  without decomposing. The conditions under which this compound is produced are not fully specified, the additive dichloro-derivative of chlorocoumarone obtained under ordinary conditions being resolved on distillation into hydrogen bromide and 1:2-dichlorocoumarone,  $C_6H_4\begin{smallmatrix} O \\ \diagup \diagdown \\ CCl \end{smallmatrix}CCl$ , which crystallises from alcohol in white leaflets melting at  $25-26^{\circ}$ , and boils at  $226-227^{\circ}$ . The authors have also obtained a *dichlorocoumarone*,  $C_8H_4OCl_2$ , and a *tetrachlorocoumarone*,  $C_8H_4OCl_4$ , of unknown constitution; these melt at  $42-43^{\circ}$  and  $131^{\circ}$  respectively, and a third *dichlorocoumarone*,  $C_8H_4OCl_2$ , probably the 1:4-derivative, melts at  $72^{\circ}$ , and boils above  $230^{\circ}$ . Chlorocoumarone boils at  $199-202^{\circ}$ , and not at  $215-217^{\circ}$ , as stated by Krämer and Spilker (Abstr., 1890, 496).

[With HELBIG.]—4-Bromocoumarone,  $C_6H_3Br\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}CH$ , prepared by heating bromosalicylaldehyde, chloroacetic acid, and alcoholic potash in sealed tubes at  $180^{\circ}$ , is a pale yellow oil with agreeable odour, boils at  $226^{\circ}$ , has a sp. gr. 1.593 at  $15^{\circ}$ , and refractive index 1.6084 at  $15^{\circ}$ .

*Bromocoumarilic acid*,  $C_6H_3\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}C \cdot CO_2H$ , produced in small quantity when the above-mentioned mixture is heated at  $198-200^{\circ}$ , is a white, crystalline powder which melts at  $253^{\circ}$  and sublimates in needles. *Bromoaldehydophenoxyacetic acid*,  $CHO \cdot C_6H_3Br \cdot O \cdot CH_2 \cdot CO_2H$ , a bye-product in the formation of 4-bromocoumarone, melts at  $163-164^{\circ}$  and sublimates in highly lustrous needles. *Bromocoumaroxyacetic acid*,  $CO_2H \cdot CH : CH \cdot C_6H_3Br \cdot O \cdot CH_2 \cdot CO_2H$ , crystallises from hot water in yellowish needles melting at  $255-256^{\circ}$ .

[With HANS BAUER.]—4-Chlorocoumarone,  $C_6H_3Cl\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}CH$ , boils at  $215-217^{\circ}$ , has a sp. gr. 1.262 at  $16^{\circ}$ , and refractive index 1.5778 at  $16^{\circ}$ . *Chloraldehydophenoxyacetic acid*,  $C_6H_4O_4Cl$ , separates from hot water in lustrous, white crystals and melts at  $169-170^{\circ}$ . 4:1-Chlorocoumarilic acid,  $C_6H_3Cl\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}C \cdot CO_2H$ , sublimates in white needles and melts at  $258^{\circ}$ . 6-Chlorocoumarone,  $C_8H_5OCl$ , boils at  $210-212^{\circ}$ .

[With GRÄFENHAN.]—1:2-Dichloro- $\beta$ -naphthalhydrofuran,



obtained on passing chlorine into a solution of  $\beta$ -naphthafuran in ether, melts at about  $74^{\circ}$ , and loses hydrogen chloride when exposed

to air; when heated with pyridine or alcoholic potash, it yields 2-chloro- $\beta$ -naphthafuran,  $C_{10}H_6\langle\begin{smallmatrix} O^- \\ CH \end{smallmatrix}\rangle CCl$ , which crystallises from alcohol in lustrous, white leaflets, and melts at  $55^\circ$ . Trichloronaphthafuran,  $C_{10}H_5OCl_3$ , prepared from  $\beta$ -naphthafuran by the action of excess of chlorine, is a white, microcrystalline powder which melts at  $144^\circ$ .

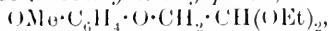
2:6(17)-Dibromo- $\beta$ -naphthafuran,  $C_{10}H_6OBr_2$ , formed when bromine acts on  $\beta$ -naphthafuran, even when the latter is in excess, crystallises from alcohol in woolly needles and melts at  $82^\circ$ ; oxidation gives rise to  $\beta$ -bromophthalic acid.

1-Chloro- $\alpha$ -naphthafuran,  $C_{10}H_7OCl$ , melts at  $47^\circ$ . The corresponding 1-bromo- $\alpha$ -naphthafuran,  $C_{10}H_7OBr$ , melts at  $76^\circ$ , and 1:8-dibromo- $\alpha$ -naphthafuran,  $C_{10}H_6OBr_2$ , crystallises from alcohol in lustrous white needles, melting at  $109^\circ$ .

Acetylcoumarone (Abstr., 1897, i, 528) combines with bromine, yielding the bromide,  $C_8H_5O\cdot CO\cdot CH_2Br$ , which melts at  $89^\circ$ ; when this is heated with the sodium derivative of salicylaldehyde, *dicoumaryl ketone*,  $CO(C_8H_5O)_2$ , is produced, and crystallises from alcohol in golden-yellow leaflets melting at  $154^\circ$ .

[With M. HELBIG.]—4-Bromo-1-acetylcoumarone,  $C_6H_3Br\langle\begin{smallmatrix} O \\ CH \end{smallmatrix}\rangle CAc$ , prepared from bromosalicylaldehyde and chloroacetone, crystallises in white needles and melts at  $109$ – $110^\circ$ ; the phenylhydrazone, *oxime*, and *semicarbazone* melt at  $164^\circ$ ,  $161^\circ$ , and  $218^\circ$ , respectively. 4-Chloro-1-acetylcoumarone,  $C_6H_3Cl\langle\begin{smallmatrix} O^- \\ CH \end{smallmatrix}\rangle CAc$ , melts at  $104^\circ$ ; the *oxime* and *phenylhydrazone* melt at  $162$ – $164^\circ$  and  $90$ – $92^\circ$  respectively.

[With A. TEUDELLOFF.]—4-Methoxycoumarone,  $OMe\cdot C_6H_3\langle\begin{smallmatrix} O^- \\ CH \end{smallmatrix}\rangle CH$ , obtained from methylacetylquinol, has a sweet, penetrating odour and boils at  $230$ – $240^\circ$ . Methylacetylquinol,



is a colourless oil which boils at  $192$ – $194^\circ$  under 38 mm. pressure, and the *aldehyde hydrate*,  $OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CH(OH)_2$ , forms silvery scales which melt at  $75$ – $76^\circ$ .

5-Methoxycoumarone,  $OMe\cdot C_6H_3\langle\begin{smallmatrix} O^- \\ CH \end{smallmatrix}\rangle CH$ , boils at  $232$ – $233^\circ$ , has a sp. gr. 1.1567 at  $16^\circ$ , and refractive index 1.5664 at  $18^\circ$ ; concentrated sulphuric acid develops an intense violet coloration. The *picrate* melts at  $64$ – $65^\circ$ . Will and Beck (Abstr., 1886, 880) obtained the same coumarone from the methyl ether of umbelliferone, but their statement that it boils at  $178$ – $180^\circ$  must be incorrect. Methylacetylresorcinol,  $OMe\cdot C_6H_3\cdot O\cdot CH_2\cdot CH(OEt)_2$ , boils at  $170$ – $172^\circ$  under 15 mm. pressure.

[With K. P. GRÄLERT.]—Whilst coumarone and its chloro-derivative are merely resinified by the action of concentrated hydrochloric acid, excess of alcoholic potash at  $180$ – $190^\circ$  gives rise to *o*-hydroxyphenylacetic acid. This compound melts at  $144$ – $145^\circ$ , and crystallises from turpentine in beautiful needles; the *barium* salt contains  $4H_2O$ , and

the *ethyl ether* melts at 103—104°. The lactone,  $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CO$ , described by Baeyer and Fritsch (Abstr., 1884, 1021), occurs in two modifications, which melt at 28.5° and 49° respectively; phosphorus oxychloride at 120° converts it into 1-chlorocoumarone which boils at 203°. The *amide* of *o*-hydroxyphenylacetic acid melts at 116—117°, and the *anilide* at 151—152°; the *hydrazide* and *phenylhydrazide* melt at 153—154° and 180° respectively. When the lactone is treated with phosphorus pentachloride, the chloride,  $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CCl_2 \end{smallmatrix} CH_2$ , is produced; elimination of hydrogen chloride from this compound gives rise to 2-chlorocoumarone, which boils at 199—201°. Other products of the action of alcoholic potash on coumarone are coumaranone, and 1- and 2-ethoxycoumarones. Alcoholic potash resolves the dichlorocoumarone which melts at 72° into 5-chloro-2-hydroxyphenylacetic acid,  $OH \cdot C_6H_3Cl \cdot CH_2 \cdot CO_2H$ , which crystallises from water in slender needles, and melts at 129.5°, the *lactone* melts at 23°.

2-Hydroxy-1-naphthylacetic acid,  $OH \cdot C_{10}H_6 \cdot CH_2 \cdot CO_2H$ , prepared by heating chloro- $\beta$ -naphthafuran with alcoholic potash at 180°, crystallises from dilute alcohol in lustrous, white leaflets, and melts at 147°; the *barium*, *calcium*, and *copper* salts are not characteristic. The *lactone*,  $C_{10}H_6 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CO$ , crystallises from alcohol in aggregates of small needles and melts at 104°.

Bromo-2-hydroxynaphthyl-1-acetic acid,  $OH \cdot C_{10}H_5Br \cdot CH_2 \cdot CO_2H$ , obtained from dibromonaphthafuran and alcoholic potash, crystallises in lustrous needles and melts at 166°; the *lactone*,  $C_{10}H_5Br \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CO$ , melts at 97° and boils at 310° under 30 mm. pressure. Sodium amalgam reduces the acid to 2-hydroxynaphthylacetic acid, melting at 147°, and alkaline potassium permanganate oxidises it to  $\beta$ -bromophthalic acid. Trichloro- $\beta$ -naphthafuran yields dichlorohydroxynaphthylacetic acid,  $C_{12}H_8O_3Cl_2$ , when heated with alcoholic potash; this acid crystallises in lustrous leaflets and melts at 194°.

*o*-Hydroxymandelic aldehyde,  $OH \cdot C_6H_4 \cdot CH(OH) \cdot CHO$ , obtained on heating coumarone dichloride with aqueous sodium acetate at 40—50° while the liquid is vigorously agitated, crystallises from water in long, white needles melting at 63—64°; ferric chloride develops a deep reddish-violet coloration, and sodium hydroxide dissolves the aldehyde, forming a yellow solution. The *semicarbazone* melts at 189—190°, and the *osazone* crystallises from alcohol and melts at 197°.

M. O. F.

**Indene, and Coumarone Resins.** By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1900, 33, 2257—2264).—When a solution of coumarone in benzene is shaken with sulphuric acid, the greater part is converted into a resin soluble in benzene, whilst the remainder separates as a brown powder. If 80 per cent. sulphuric acid is employed, the soluble resin is almost exclusively obtained, but the yield of the insoluble resin increases with the concentration of the acid, until, with

95 per cent. acid, the coumarone is precipitated in the latter form nearly quantitatively. The pure soluble resin melts at  $107-108^{\circ}$ , and has a sp. gr.  $1.25$  at  $19^{\circ}$ ; its composition,  $C_8H_6O$ , is identical with that of coumarone, but its molecular weight is four times as great. When this resin is heated at  $300-350^{\circ}$ , a distillate is obtained consisting mainly of coumarone, together with some phenol, ethylbenzene, and small quantities of *o*-ethylphenol, benzene, toluene, and hydro-coumarone.

By the action of sulphuric acid (75 per cent.) on indene, it is converted into a resin which is soluble in benzene; this resin has the same composition as indene itself, but a variable melting point and molecular weight. The white resin obtained in this way melts at  $210^{\circ}$ . Under certain conditions, a *compound* of indene with sulphuric acid can be isolated; its barium salt,  $(C_8H_6 \cdot OSO_3)_2Ba$ , forms yellow, indistinctly crystalline plates. The indene resin decomposes at  $290-340^{\circ}$ , yielding a distillate which consists of indene, together with some hydrindene and phenol.

The polymerisation of coumarone proceeds with very little rise of temperature, whilst that of indene produces considerable development of heat; in both cases, it can also be effected by means of aluminium chloride.

If crude, heavy benzene, boiling at  $155-185^{\circ}$ , is treated with sulphuric acid and the resulting mixture of resins distilled, a fraction is obtained at  $168-172^{\circ}$  which consists of coumarone and hydrindene; the coumarone may be separated as the picrate, and can be more easily obtained in this manner than directly from the heavy benzene. The greater part of the indene, however, is decomposed. E. G.

**Esterification of Unsymmetrical Polybasic Acids. I. Esterification of Nitroterephthalic Acid.** By RUDOLF WEGSCHIEDER (*Monatsh.*, 1900, 21, 621-637. Compare Abstr., 1895, ii, 310; 1898, i, 30 and 238).—Good yields of nitroterephthalic acid may be obtained by Burkhardt's method (*Ber.*, 1877, 10, 145), even when as much as 20 grams of terephthalic acid are employed in one operation. The nitro-acid melts at  $259.5^{\circ}$  (corr.) and the normal methyl ester at  $74-75^{\circ}$ . The *acid potassium salt*,  $C_8H_4O_6NK \cdot H_2O$ , *silver salt*,  $C_8H_3O_6NAg_2$ , and *lead salt*,  $C_8H_3O_6NPb \cdot 3H_2O$ , have been prepared. The normal methyl ester is obtained by the action of methyl iodide on the acid potassium salt, or of methyl alcohol on the acid alone or in presence of hydrochloric or sulphuric acid. It crystallises in triclinic prisms [ $a:b:c = 1.4745:1:0.52248$ ;  $a = 100.516'$ ,  $\beta = 98^{\circ}10'2''$ ,  $\gamma = 107^{\circ}14'8''$ ].

The normal *n-propyl ester* is a colourless, mobile liquid distilling at  $228-230^{\circ}$  (corr.) under 18 mm. pressure, and does not solidify at  $0^{\circ}$ . When benzyl alcohol and nitroterephthalic acid are heated together, benzaldehyde and *benzyl aminoterephthalate* are formed; the latter crystallises in needles melting at  $99-101^{\circ}$ , and forms a *hydrochloride* which is insoluble in ether. When the alcohol and acid are heated in the presence of sulphuric acids, the products are benzyl ether, and probably azo- and amino-terephthalic acids. The acid is also reduced to the amino-acid when heated with menthol. J. J. S.

**Esterification of Unsymmetrical Polybasic Acids. II. Esterification of Bromo- and Hydroxy-terephthalic Acids.** By RUDOLF WEGSCHEIDER and KARL BITTNER (*Monatsh.*, 1900, **21**, 638—654. Compare preceding abstract).—Bromoterephthalic acid has been obtained by Sandmeyer's method from the amino-acid and hydroxyterephthalic acid by Burkhardt's method (*Ber.*, 1877, **10**, 145). When the acid potassium salts of the two acids are treated with methyl iodide,  $\alpha$ -acid esters are formed, and the rule previously enunciated is followed. By the esterification of the bromo-acid, normal and  $\beta$ -acid esters are formed; with the hydroxy-acid, the normal ester alone is produced when hydrochloric acid or much sulphuric acid is employed, but with only a small amount of sulphuric acid the  $\beta$ -acid ester is also obtained. When the normal ester of the bromo-acid is hydrolysed by alkali, the  $\alpha$ -acid ester is formed, but from the normal ester of the hydroxy-acid the  $\beta$ -acid ester is obtained.

In the esterification, the same acid ester is obtained, whether the catalytic or autocatalytic method is employed. Methyl bromoterephthalate,  $C_6H_3Br(CO_2Me)_2$ , melts at  $54^\circ$ ; both  $\alpha$ - [ $CO_2H : Br : CO_2Me = 1 : 2 : 4$ ] and  $\beta$ - [ $CO_2Me : Br : CO_2H = 1 : 2 : 4$ ] methyl hydrogen terephthalate crystallise in glistening needles from their aqueous solutions, dissolve readily in most organic solvents, the  $\alpha$ -compound is somewhat more sparingly soluble in cold water than the  $\beta$ -, and its neutral solution gives a precipitate with lead acetate which is soluble in excess and not reprecipitated on boiling; the  $\beta$ -compound behaves similarly, except that the precipitate is thrown down again on boiling. Slight differences with copper sulphate and silver nitrate solutions are also observable. The constitutions of the two compounds follow from their electrical conductivities (compare Wegscheider, *Abstr.*, 1895, ii, 310).  $\alpha$ -Methyl hydrogen terephthalate melts at  $145^\circ$  and has the dissociation constant  $K$  0.037; the  $\beta$ -acid ester melts at  $164^\circ$  and has  $K$  0.50.

$\alpha$ -Methyl hydrogen hydroxyterephthalate, [ $CO_2Me : OH : CO_2H = 1 : 2 : 4$ ], crystallises in needles, melts at  $206$ — $208^\circ$ , is readily soluble in ether, alcohol, or warm benzene, but is not so readily soluble in chloroform as the isomeride, and gives a reddish-yellow colour with ferric chloride.

$\beta$ -Methyl hydrogen hydroxyterephthalate [ $CO_2H : OH : CO_2Me = 1 : 2 : 4$ ] melts at  $177^\circ$ , and gives a purple colour with ferric chloride.

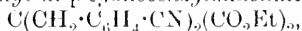
J. J. S.

***p*-Cyanobenzyl Chloride.** By NATHAN MOSES (*Ber.*, 1900, **33**, 2623—2630. Compare Mellinshoff, *Abstr.*, 1890, 239; Günther, *ibid.*, 977; Reinglass, 1891, 1344; and Banse, 1894, i, 574).—The reactions between various reagents and *p*-cyanobenzyl chloride have been studied, and the products isolated. *p*-Cyanobenzyl thiocyanate,  $CN \cdot C_6H_4 \cdot CH_2 \cdot SCN$ , forms glistening needles melting at  $85$ — $86^\circ$ , and when heated with concentrated hydrochloric acid at  $180^\circ$  yields benzylsulphide-*p*-dicarboxylic acid,  $S(CH_2 \cdot C_6H_4 \cdot CO_2H)_2$ , the nitrile of which, obtained by the action of potassium hydrogen sulphide on *p*-cyanobenzyl chloride, crystallises in yellowish plates melting at  $114.5^\circ$ . A good yield of *p*-cyanocinnamic acid melting at  $248$ — $249^\circ$  is obtained when *p*-cyanobenzaldehyde, potassium acetate and acetic acid are heated, but when sodium acetate is employed a small amount



of a substance melting at  $165^{\circ}$ , and probably *p*-aldehydobenzamide is the only product. *p*-Cyanophenylpropionic acid crystallises in six-sided prisms melting at  $135$ — $136^{\circ}$ , and on hydrolysis yields the dibasic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which decomposes at  $280^{\circ}$ . Ethyl di-*p*-cyanobenzylacetate,  $\text{C}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2\cdot\text{CO}_2\text{Et}$ , crystallises in needles melting at  $133$ — $134^{\circ}$ .

Ethyl di-*p*-cyanobenzylacetate,  $\text{CN}\cdot\text{C}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2\cdot\text{CO}_2\text{Et}$ , obtained from ethyl sodiocyanoacetate, melts at  $110.5^{\circ}$ , and on hydrolysis yields di-*p*-carboxybenzylacetic acid,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , melting at  $270$ — $271^{\circ}$ . Ethyl di-*p*-cyanobenzylmalonate,



melts at  $194^{\circ}$ , and when hydrolysed yields the tribasic acid melting at  $270$ — $271^{\circ}$ . *p*-Cyanodiphenylmethane, obtained from *p*-cyanobenzyl chloride, benzene, and aluminium chloride, crystallises in prisms melting at  $50$ — $51^{\circ}$ , and on hydrolysis gives diphenylmethane-*p*-carboxylic acid,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , melting at  $157$ — $158^{\circ}$ . *p*-Cyanophenyltolylmethane is an oil distilling at  $198$ — $199^{\circ}$  under 15 mm. pressure. Phenyltolylmethane-*p*-carboxylic acid,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , crystallises in colourless needles melting at  $134$ — $135^{\circ}$ .

Di-*p*-cyanodibenzylamine,  $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2$ , obtained by shaking *p*-cyanobenzyl chloride with 10 per cent. alcoholic ammonia, crystallises in prisms melting at  $105$ — $106^{\circ}$ , and on hydrolysis with hydrochloric acid yields di-*p*-carboxybenzylamine hydrochloride, which melts above  $280^{\circ}$ . Tri-*p*-cyanotribenzylamine hydrochloride,  $\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_3\cdot\text{HCl}$ , crystallises in acicular groups decomposing between  $270^{\circ}$  and  $280^{\circ}$ .

O. Fischer's *p*-cyanotriphenylmethane may be obtained from cyanobenzylidene chloride, benzene, and aluminium chloride. J. J. S.

**Transformation of Coloured Unsaturated Dicarboxylic Acids into Colourless Stereoisomerides.** By HANS STOBIE (*Chem. Centr.*, 1900, ii, 561—562; from *Verh. Ver. Deutsch. Naturf. Aerzte*, 1899, 88—90).—Dibenzylidenesuccinic acid,  $\text{C}_2(\text{CHPh})_2(\text{CO}_2\text{H})_2$ , prepared by the action of sodium ethoxide, free from alcohol, on an ethereal solution of benzaldehyde (2 mols.) and ethyl succinate (1 mol.), melts at  $218^{\circ}$ ; on oxidation, it yields benzaldehyde and oxalic acid, and on reduction dibenzylsuccinic acid,  $\text{C}_{18}\text{H}_{18}\text{O}_4$ . Dibenzylidenesuccinic anhydride is a lemon-yellow substance, which melts at  $203$ — $204^{\circ}$ , and when treated with resorcinol forms a compound analogous to fluorescein which by the action of bromine yields an eosin. By exposing solutions of the anhydride in benzene containing iodine to the action of sunlight, the stereoisomerides of dibenzylidenesuccinic acid are obtained in the form of their anhydrides. *iso*Dibenzylidenesuccinic anhydride separates in granules and melts at  $254$ — $255^{\circ}$ . *allo*Dibenzylidenesuccinic anhydride forms small scales and melts at  $223^{\circ}$ . Both are colourless substances and very sparingly soluble in benzene. In one case an anhydride melting at  $172$ — $175^{\circ}$  was obtained, but by the further action of light it was converted into the *iso*anhydride. The acids corresponding with the anhydrides are also colourless compounds. *iso*Dibenzylidenesuccinic acid loses water before it melts; *allo*dibenzylidenesuccinic acid melts at  $203$ — $210^{\circ}$  and decomposes at  $220^{\circ}$ .

Acids of similar constitution are formed by condensing  $\gamma$ -disubstituted ethyl itaconate with aldehydes and ketones in presence of sodium ethoxide.  $\gamma$ -Diphenyl- $\alpha$ -benzylideneitaconic acid,  $C_{24}H_{18}O_4$ , prepared from benzaldehyde and ethyl diphenylitaconate, is a yellow substance and melts and decomposes at  $218-219^\circ$ . By exposing benzene solutions of the acid or of the red anhydride containing iodine to the action of sunlight, a heavy, colourless acid and a heavy, colourless anhydride are formed respectively; the latter melts at  $267^\circ$ . A third colourless isomeride melting at  $247^\circ$  is also formed.

From these experiments it is evident that the colour of all these compounds may stand in some fixed relationship to their configuration in space.

E. W. W.

**Coloured Sulphur Compounds of the Diphenyl- and Triphenyl-methane series.** I. By RICHARD E. MEYER (*Ber.*, 1900, **33**, 2570—2576).—By fusion with sodium sulphide, fluorescein is converted into 1-thiofluorescein, in which the oxygen of the pyrone ring is replaced by sulphur, whereas fluoran, in which no hydroxyl groups are present, does not react in this way. On the other hand, by the action of phosphorus pentasulphide, the carbonyl and lactone oxygen of fluoran, diphenylphthalide, xanthone, and thioxanthone, are readily replaced by sulphur, whilst this reaction only occurs very imperfectly or not at all with fluorescein and similar derivatives. No definite relation could be established between the degree of fluorescence of the compound and the number and position of the sulphur atoms present, and similar irregularities are presented by the melting points of these compounds. The thiolactones and thioketones yielded by colourless ketones and lactones are strongly coloured, and this affords additional evidence of the marked chromophoric function of the sulphur atom.

The experimental details are given in the following abstract.

A. H.

**Coloured Sulphur Compounds of the Diphenyl- and Triphenyl-methane Series.** II. By RICHARD E. MEYER and J. SZANECKI (*Ber.*, 1900, **33**, 2577—2584. Compare preceding abstract).

—Dithiofluoran,  $CS\langle\begin{smallmatrix} C_6H_4 \\ -S- \end{smallmatrix}\rangle C\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle O$ , is formed when fluoran is heated with phosphorus pentasulphide, and crystallises in thick red needles, melting at  $155-156^\circ$ . Alcoholic soda reconverts it into fluoran, and on distillation with lime it yields xanthone, so that the sulphur atoms must be situated in the lactone ring. In sulphuric acid solution, it shows a very faint green fluorescence. Dithiofluorescein chloride (dichlorodithiofluoran),  $CS\langle\begin{smallmatrix} C_6H_4 \\ -S- \end{smallmatrix}\rangle C\langle\begin{smallmatrix} C_6H_3Cl \\ C_6H_3Cl \end{smallmatrix}\rangle O$ , is formed by the action of phosphorus pentasulphide on fluorescein chloride, and crystallises in light red needles melting at  $196-197^\circ$ . Diphenylphthalide also reacts with phosphorus pentasulphide, yielding dithiodiphenylphthalide,  $CS\langle\begin{smallmatrix} C_6H_4 \\ -S- \end{smallmatrix}\rangle CPh_2$ , which forms brick-red prisms melting at  $161-162^\circ$ . Xanthone is converted by the same reagent into xanthione,  $CS\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle O$  (Graebe and Roeder, *Abstr.*, 1899,

i, 705), whilst thioxanthone yields *dithioxanthone* (thioxanthione),  $\text{CS} \langle \text{C}_6\text{H}_4 \rangle \text{S}$ , which is a yellow powder and melts and decomposes at  $215^\circ$ . The solution in sulphuric acid has a reddish-brown colour, and possesses a distinct yellow fluorescence.

Thiofluorescein has been already described by Wyler (*Diss.*, Zurich, 1894); it dissolves in alkalis, forming a rose-pink solution with a faint green fluorescence. Phosphorus pentabromide converts it into *thiofluorescein bromide*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{C}_6\text{H}_3\text{Br} \rangle \text{S}$ , which is a brown powder melting at  $252^\circ$ . A. H.

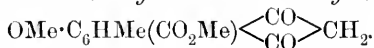
**Mixed Esters of Cochinelic Acid.** By JOSEF LANDAU (*Ber.* 1900, 33, 2442—2446).—When cochinelic acid (compare Liebermann and Voswinckel, *Abstr.*, 1897, i. 539) in ammoniacal solution is precipitated with lead acetate, a *dilead* salt,  $\text{C}_{10}\text{H}_4\text{O}_7\text{Pb}_2$ , is obtained. This, however, reacts with methyl iodide just as the trisilver salt does.

When dry trisilver cochinelate is heated with excess of methyl iodide at  $100^\circ$ , a mixture of the *methyl ethers* of *trimethyl* and *dimethyl hydrogen cochinelate*,

$\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me})_3$  and  $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{H})(\text{CO}_2\text{Me})_2$ , is obtained; these can be separated by means of aqueous sodium carbonate. The yield of trimethyl ester is comparatively small; it can be increased greatly by using, instead of the pure silver salt, a mixture of it with silver oxide, obtained by precipitating with silver nitrate a solution of 1 mol. of cochinelic acid in 4 mols. of aqueous potassium hydroxide. The trimethyl ester melts at  $111$ — $113^\circ$ , the dimethyl ester at  $58$ — $62^\circ$  when dried in the air, at  $85$ — $87^\circ$  when dried in a vacuum desiccator, in which it effloresces; neither ester gives a colour reaction with ferric chloride. When the dimethyl ester (1 mol.), best mixed with silver oxide in excess, is heated at  $100^\circ$  with methyl alcoholic potassium methoxide (1 mol.) and methyl iodide, it is converted into the trimethyl ester. When these esters are treated either with 5 per cent. aqueous barium hydroxide or with 25 per cent. aqueous potassium hydroxide, the methoxyl group is hydrolysed as well as the carbomethoxyl groups, and cochinelic acid is obtained at once. The unusually ready passage from the OH to the OMe group, and *vice versa*, is noteworthy. C. F. B.

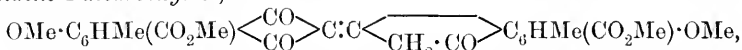
**Diketohydrindene Derivatives of Cochinelic Acid.** By JOSEF LANDAU (*Ber.*, 1900, 33, 2446—2453). When trimethylcochinelate methyl ether,  $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me})_3$  (preceding abstract), is heated at  $100^\circ$  with metallic sodium, and methyl acetate is added gradually, a yellow *sodium* derivative,  $\text{C}_{13}\text{H}_{13}\text{O}_7\text{Na}$ , which crystallises with  $11\frac{1}{2}\text{H}_2\text{O}$ , is formed. When an aqueous solution of this salt is acidified, the sodium is removed and *dimethyl 5-methoxy-7-methyl-1:3 diketohydrindene-2:4-dicarboxylate*,  $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me}) \langle \text{C} \rangle \text{CH} \cdot \text{CO}_2\text{Me}$ , is precipitated. This forms an orange-yellow powder which melts and decomposes at  $98$ — $100^\circ$ , and gives a reddish-brown coloration with ferric

chloride; in ethereal solution it decomposes gradually, forming *methyl 5-methoxy-7-methyl-1:3-diketohydrindene-4-carboxylate*,



This melts and decomposes at 160—161°; it dissolves in alkalis; when heated with protocatechualdehyde at 150°, it condenses to *methyl 2-m-p-dihydroxybenzylidene-5-methoxy-7-methyl-1:3-diketohydrindene-4-carboxylate*,  $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me}) \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , which is brownish-yellow, melts at 264—266°, dyes mordants, and dissolves in alkalis.

When the yellow sodium derivative is heated with fuming hydrochloric acid at 100°, *dimethyl anhydrobis-5-methoxy-7-methyldiketohydrindene-4-dicarboxylate*,



is produced. This forms yellow crystals, melts at 243—244°, dissolves in alkalis, and does not dye mordants; when heated with methyl alcoholic potassium methoxide at 100°, it yields the *acid* or the *methyl hydrogen ester*, according as the alkali is used in excess or not; attempts to hydrolyse the methoxyl groups were unsuccessful. The methyl hydrogen ester melts at 222—223°, the acid melts and decomposes at 294—296°; both form yellow crystals, dissolve in alkalis, and give coloured precipitates with salts of heavy metals. C. F. B.

**Constitution of Usnic Acid.** By EMANUELE PATERNÒ (*Atti. Real. Accad. Lincei*, 1900, [v], 9, ii, 119—132. Compare Widman, this vol., i, 235, 347).—An historical account is given of the chemistry of usnic acid, the results of Widman (*loc. cit.*) and of Hesse being criticised. The following are the new results obtained by the author.

*Benzoylusnic acid*,  $\text{C}_{15}\text{H}_{15}\text{O}_7 \cdot \text{Bz}$  or  $\text{C}_{18}\text{H}_{16}\text{O}_8 \cdot \text{Bz}$ , obtained by heating a dilute potassium hydroxide solution of the acid with benzoyl chloride, separates from alcohol, ethyl acetate, or benzene in lustrous, orange-yellow, monoclinic prisms melting at 218—220°. [ $a:b:c = 1.9458:1:0.9340$ ;  $\beta = 56^\circ 25' 30''$ ]. The *oxime*,  $\text{C}_{18}\text{H}_{15}\text{O}_6\text{N}$ , melts at 226—228°, and is soluble in alcohol or acetic acid. By the action of phenylhydrazine on the acid in acetic acid solution, a *phenylhydrazone* of an anhydro-acid of the composition  $\text{C}_{24}\text{H}_{22}\text{O}_6\text{N}_2$  or  $\text{C}_{24}\text{H}_{20}\text{O}_5\text{N}_2$  is obtained, melting at 194—195°; it does not yield usnic acid on treatment with acetic and sulphuric acids, as was the case with the compound prepared by Widman (*loc. cit.*). On heating decarbusnein with sodium acetate and acetic anhydride, the diacetyl derivative of decarbusnic acid is formed, from which it is concluded that the molecule of usnic acid contains an acetyl radicle. Usnic acid, prepared by heating usnic acid with sulphuric acid, may also be obtained by treating decarbusnein in the same way. The basicity of usnic and decarbusnic acids is discussed, the constitutions given by Widman being regarded as erroneous; Widman's observation that usnic acid is optically active is confirmed. T. H. P.

**Oxidation with Atmospheric Oxygen.** By HEINRICH BILTZ (*Ber.*, 1900, 33, 2295—2299).—When a stream of air is passed through

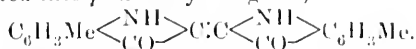
a solution of dibromo-*p*-hydroxybenzaldehyde, phenylhydrazine and potassium hydroxide, *tetrabromodihydroxybenzilazone*,  $C_{25}H_{20}O_2N_4Br_4$ , is obtained as a crystalline powder; it melts at  $206^\circ$ , and dissolves in warm acetic acid or alcohol, but is only sparingly soluble in light petroleum, chloroform, benzene, or water. An equivalent quantity of hydrogen peroxide is simultaneously produced. E. G.

**Halogenised Aromatic Amino-ketones.** By FRANZ KUNCKELL (*Ber.*, 1900, 33, 2644—2654).—[With G. TREUTLER.]—*p*-Chloroacetylacetanilide,  $CH_2Cl \cdot CO \cdot C_6H_4 \cdot NHAc$ , made by the action of aluminium chloride on a mixture of acetanilide and chloroacetyl chloride (compare following abstract), crystallises from a mixture of chloroform and alcohol in small, white needles, is sparingly soluble in alcohol or water, but readily in chloroform, and melts at  $212^\circ$ . It yields *p*-acetylaminobenzoic acid when oxidised with potassium permanganate. *p*-Chloroacetylaniline,  $CH_2Cl \cdot CO \cdot C_6H_4 \cdot NH_2$ , crystallises in yellow or reddish-yellow leaflets, melts at  $147^\circ$ , and dissolves readily in alcohol and less readily in ether or benzene.

*p*-Acetylaminobenzoylmethyl acetate,  $CH_3 \cdot CO_2 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot NHAc$ , made by heating *p*-chloroacetylaniline dissolved in alcohol with potassium acetate, crystallises from water in small, white needles melting at  $162^\circ$ . The corresponding benzoate,  $C_6H_5 \cdot CO_2 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot NHAc$ , forms white, felted needles and melts at  $200$ — $201^\circ$ . *p*-Aminobenzoylmethyl acetate crystallises from benzene in white needles and melts at  $135^\circ$ .

*p*-Acetylaminobenzoylcarbinol,  $OH \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot NHAc$ , obtained by shaking the acetate with 15 per cent. sodium hydroxide solution, crystallises in white leaflets, melts at  $176$ — $177^\circ$ , and dissolves readily in chloroform and alcohol, but is nearly insoluble in ether or benzene. The phenylhydrazone,  $C_{16}H_{17}O_2N_3$ , separates from alcohol in yellow needles melting at  $223^\circ$ . *p*-Aminobenzoylcarbinol crystallises from benzene in bright yellow needles melting at  $165^\circ$ , and is soluble in alcohol or in acids, but only very sparingly in water. The hydrochloride,  $C_8H_9O_2N \cdot HCl$ , melts above  $250^\circ$ , and the phenylhydrazone,  $C_{11}H_{17}ON_3$ , crystallises in yellow needles and melts at  $199^\circ$ .

When aceto-*p*-toluidide is treated with chloroacetic chloride, both the chloroacetyl-*o*- and *m*-toluidines are obtained. Chloroacetylaceto-*p*-toluidide,  $CH_2Cl \cdot CO \cdot C_6H_3Me \cdot NHAc$ , separates from alcohol in white needles melting at  $180$ — $181^\circ$ , and dissolves readily in alcohol, ether, chloroform, benzene, or light petroleum; when warmed with potassium hydroxide solution, it is, as a result of hydrolysis and oxidation, partially converted into *p*-dimethylindigotin,

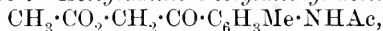


Chloroacetyl-*p*-toluidine melts at  $136^\circ$ .

Chloroacetylaceto-*m*-toluidide crystallises from dilute alcohol in yellow, cube-like crystals melting at  $120^\circ$ , dissolves readily in alcohol, chloroform, or benzene, and sparingly in ether or light petroleum. Chloroacetyl-*m*-toluidine,  $CH_2Cl \cdot CO \cdot C_6H_3Me \cdot NH_2$ , melts at  $75^\circ$ .

[With G. HECKER.]—Chloroacetyl-*o*-toluidine, from aceto-*o*-toluidide,

crystallises from alcohol in slender, white needles and melts at  $160^{\circ}$ ; when warmed with strong aqueous potash, it is not oxidised to an indigo derivative, so that the chloroacetyl group is not in the ortho-position with regard to the acetyl-amino-group; it is oxidised by permanganate to a dicarboxylic acid,  $C_{10}H_9O_5N$ , of unknown constitution; on nitration, it yields a *mononitro*-derivative,  $C_{11}H_{11}O_4N_2Cl$ , which melts at  $205^{\circ}$ . *Acetyl-amino-o-tolylmethyl acetate*,



crystallises from alcohol in white needles and melts at  $90^{\circ}$ ; the corresponding *benzoate*,  $C_{18}H_{17}O_4N$ , forms white needles and melts at  $130^{\circ}$ . *Chloroacetyl-o-toluidine*,  $CH_2Cl \cdot CO \cdot C_6H_3Me \cdot NH_2$ , separates from alcohol in white leaflets melting at  $75^{\circ}$ ; the *hydrochloride*,  $C_9H_{11}ONCl_2$ , decomposes at about  $170^{\circ}$ .

*Chloroacetyl-as-aceto-m-xylylidide*,  $C_{12}H_{14}O_2NCl$ , crystallises from alcohol, in which it is readily soluble, in long, white needles melting at  $150^{\circ}$ . *Chloroacetyl-as-m-xylylidine*,  $CH_2Cl \cdot CO \cdot C_6H_3Me_2 \cdot NH_2$ , melts at  $126^{\circ}$ ; its *hydrochloride* forms long, white needles which decompose without melting at  $150^{\circ}$ . *Chloroacetylnitroxylylidine*,  $C_{12}H_{13}O_4N_2Cl$ , crystallises from alcohol and melts at  $202^{\circ}$ .

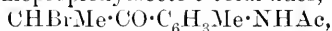
*p-Amino-m-dimethylbenzoylmethyl acetate*,  $C_{12}H_{15}O_3N$ , from *chloroacetyl-as-m-xylylidine*, crystallises in yellowish leaflets melting at  $109^{\circ}$ , and the corresponding *benzoate* forms needles melting at  $118-119^{\circ}$ . The free carbinol could not be obtained.

*Chloroacetylaceto-ψ-cumidide*,  $CH_2Cl \cdot CO \cdot C_6HMe_3 \cdot NHAc$



crystallises from dilute alcohol in white needles melting at  $189^{\circ}$ . *Chloroacetyl-ψ-cumidine*,  $CH_2Cl \cdot CO \cdot C_6HMe_3 \cdot NH_2$ , crystallises from water in pearly leaflets and melts at  $70^{\circ}$ ; the *hydrochloride* forms white needles melting at  $245^{\circ}$ . *Chloroacetylnitroaceto-ψ-cumidide*,  $C_{13}H_{15}O_4N_2Cl$ , crystallises from alcohol in white, felted needles and melts at  $200^{\circ}$ .

Two isomeric bromopropionylaceto-o-toluidides,



were obtained by treating a mixture of aceto-o-toluidide and bromopropionyl bromide with aluminium chloride in direct sunlight; the one forms bundles of white needles melting at  $158^{\circ}$ , and the other small, white needles melting at  $138^{\circ}$ .

*α-Bromopropionylacetoxylylidide*,  $C_{13}H_{16}O_2NBr$ , crystallises from alcohol in white leaflets melting at  $115-116^{\circ}$ .

*α-Bromopropionylaceto-ψ-cumidide*,  $C_{14}H_{15}O_2NBr$ , separates from dilute alcohol in a crystalline condition and melts at  $146^{\circ}$ . A. L.

**New Method of Preparing Aromatic Amino-ketones.** By FRANZ KUNCKELL (*Ber.*, 1900, 33, 2641—2644).—A good general method of preparing aromatic amino-ketones consists in allowing aluminium chloride to act on a mixture of acetanilide and an acyl chloride, carbon disulphide being used as a diluent. The resulting acetyl compounds are afterwards hydrolysed by boiling with 15 per cent. hydrochloric acid.

*p-Propionylacetanilide*,  $COEt \cdot C_6H_4 \cdot NHAc$ , crystallises from water

in yellow needles melting at  $161^{\circ}$ . *p*-Propionylaniline is soluble in water and alcohol, crystallises in long, yellow needles, and melts at  $140^{\circ}$ ; the *hydrochloride* and *sulphate* form white crystals and melt at  $198^{\circ}$  and  $225^{\circ}$  respectively.

*p*-n-Butyrylacetanilide,  $\text{COPr}^{\text{a}} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$ , crystallises in white needles and melts at  $142^{\circ}$ . *p*-n-Butyrylaniline dissolves readily in alcohol and water and melts at  $84^{\circ}$ ; the *hydrochloride* melts at  $178^{\circ}$ , and the *sulphate* at  $216^{\circ}$ .

*Ethyl p*-propionylphenylcarbamate,  $\text{COEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , crystallises in white needles and melts at  $154^{\circ}$ . *p*-Propionylphenylcarbamide,  $\text{COEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , melts at  $218^{\circ}$ . A. L.

**New Synthesis of Ketones.** By EDGAR WEDEKIND (*Chem. Centr.*, 1900, ii, 561; from *Verh. Ver. Deutsch. Naturf. Aerzte*, 1899, 108—110).—By the action of phenylacetyl chloride on triethylamine dissolved in anhydrous ether or benzene, triethylamine hydrochloride and a compound,  $(\text{CHPh} \cdot \text{CO})_x$ , are formed, no intermediate additive compound being produced. The crude product is a thick oil, and on distillation under 8—10 mm. pressure yields a clear, yellow oil from which a crystalline oxime may be prepared. The ketone obtained from the oxime yields a phenylhydrazone identical with that formed by the action of phenylhydrazine on the crude oil. From the crude product, however, a ketone of a different constitution has been isolated; it is a crystalline substance and melts at  $170$ — $171^{\circ}$ . The formation of dehydracetic acid by the action of acetyl chloride on triethylamine is probably due to the polymerisation of a ketone. Since many acid haloids also form primary products which react with water to form corresponding acid anhydrides, this action may possibly constitute a new method of preparing ketones. E. W. W.

**3-Bromo-1-indone and its Derivatives.** By S. SCHLOSSBERG (*Ber.*, 1900, 33, 2425—2432).—3-Bromo-1-indone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CBr} \end{smallmatrix} \text{CH}$ , prepared by distilling phenylpropionic acid hydrobromide with phosphoric oxide in a vacuum, forms small, yellow needles and melts at  $64^{\circ}$ ; bromine converts it into dibromoindone, and strong nitric or sulphuric acid into dibromodiketohydrindene.

3-Anilino-1-indone,  $\text{CO} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{NHPh}$ , crystallises from alcohol in bronze-coloured, metallic flakes and melts with decomposition at  $204$ — $205^{\circ}$ . 3-Benzylamino-1-indone,  $\text{CO} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}$ , crystallises from alcohol in orange needles and melts at  $153^{\circ}$ . These two compounds are converted by fuming hydrochloric acid into diketohydrindene. 3-Bromo-1-indosime,  $\text{CBr} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{OH}$ , crystallises from dilute alcohol in minute, yellow needles and melts at  $98^{\circ}$ . 3-Phenylhydrazino-1-indonephenylhydrazone,



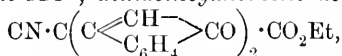
or  $\text{NHPh} \cdot \text{N} : \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{NHPh}$ , forms small, reddish-brown

needles and melts and decomposes at  $142^{\circ}$ . *Diindoneacetic acid*,  $\text{CH}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2 \cdot \text{CO}_2\text{H}$ , prepared by the action of sodium ethoxide on a mixture of ethyl malonate and bromoindone, crystallises from alcohol in small, yellow needles and melts at  $192^{\circ}$ ; the *sodium* salt is orange-coloured, and only slightly soluble in water and alcohol.

*Diindoneacetone*,  $\text{CHAc}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$ , prepared by the action of ethyl sodioacetoacetate on 3-bromoindone, crystallises from alcohol in small, dull yellow needles and melts at  $212^{\circ}$ .

*Diindoneacetophenone*,  $\text{CHBz}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$ , prepared by the action of ethyl sodiobenzoylacetate on 3-bromoindone, crystallises from alcohol in small, glistening, yellow needles and melts at  $246^{\circ}$ .

*Ethyl indonecyanoacetate*,  $\text{CO} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , prepared by the action of sodium ethoxide on 3-bromoindone and ethyl cyanoacetate in the cold, crystallises from dilute alcohol in small, brown needles and melts at  $124^{\circ}$ ; *diindonecyanoacetic acid*,



produced when hot solutions are used, crystallises from alcohol in small, glistening, dark yellow needles and melts and decomposes at  $285^{\circ}$ ; the sodium salt is orange-red and only slightly soluble in water.

*Diindonemalonitrile*,  $\text{C}(\text{CN})_2(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$ , crystallises from acetic acid in small, reddish-brown needles and melts with decomposition at  $310^{\circ}$ . *Diindonebenzoylacetone*,  $\text{CAcBz}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$ , crystallises from alcohol in small, yellow needles and melts at  $258^{\circ}$ .

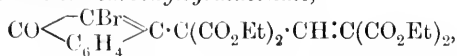
T. M. L.

**Halogen-substituted Indone Derivatives of  $\beta$ -Diketones.** By THEODOR LANSER and FRITZ WIEDERMANN (*Ber.*, 1900, 33, 2418—2424. Compare Liebermann, *Abstr.*, 1899, i, 373 and 522).—*Chloroindone-malononitrile*,  $\text{CO} \begin{smallmatrix} \text{CCl} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{CH}(\text{CN})_2$ , crystallises from dilute acetic acid in reddish-brown needles and melts with frothing at  $159^{\circ}$ .

*Chloroindonecyanoacetamide*,  $\text{CO} \begin{smallmatrix} \text{CCl} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$ , crystallises from alcohol in white, but from acetic acid in yellow, needles, and melts at  $208$ — $209^{\circ}$ .

*Ethyl bischloroindonemalonate*,  $\text{C}_2(\text{C} \begin{smallmatrix} \text{CCl} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2(\text{CO}_2\text{Et})_4$ , prepared by the action of moist silver oxide on ethyl chloroindonemalonate, crystallises in minute, white needles and melts at  $219$ — $220^{\circ}$ .

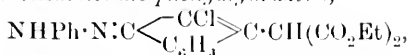
*Ethyl bromoindonedicarboxyglutaconate*,



crystallises from alcohol in yellow needles and melts at  $131^{\circ}$ .



*Ethyl chloroindonemalonate phenylhydrazone*,



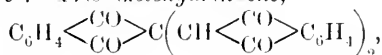
forms short, brown needles and melts at 144–145°.

*Bromoindone resorcinol ether*,  $\text{CO} \begin{array}{c} \text{CBr} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , forms yellow needles and melts at 171°; the *acetyl* derivative separates from dilute acetic acid in yellow crystals and melts at 105°.

*Ethylaminochloroindone*,  $\text{CO} \begin{array}{c} \text{CCl} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \cdot \text{NHEt}$ , prepared by the action of ethylamine on the ethyl malonate derivative, forms short, red needles and decomposes at 188°. *Ethylaminobromoindone* forms red needles and decomposes at 151°. *Benzylaminochloroindone*,  $\text{CO} \begin{array}{c} \text{CCl} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}$ , forms red prisms and decomposes at 182°. Attempts to condense dibromoindone with 2 mols. of ethyl malonate gave only Gabriel and Michael's tribenzoylenebenzene (compare Liebermann and Bergami, Abstr., 1890, 514).

T. M. L.

**Action of Iodine on Ethyl Sodiodiketohydrindenecarboxylate.** By CARL LIEBERMANN and L. FLATOW (*Ber.*, 1900, 33, 2433–2439).—*Diiododiketohydrindene*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} > \text{CI}_2$ , prepared by the action of iodine on ethyl sodiodiketohydrindenecarboxylate, crystallises from acetic acid in small, yellow prisms and melts and decomposes at 199°. *Trisdiketohydrindene*,



produced under other conditions when less iodine is used, forms snow-white prisms and melts and decomposes at 266°; the *dipotassium* salt (of the enolic form) is green with a golden shimmer; the *barium* salt is red. *Anhydrottrisdiketohydrindene*,  $\text{C}_{27}\text{H}_{12}\text{O}_5$ , probably a pyrone

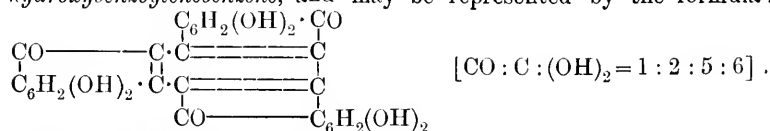
derivative,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} > \text{C} \begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{C} = \text{C} \\ | \\ \text{C} = \text{C} \\ | \\ \text{CO} \cdot \text{C}_6\text{H}_4 \end{array} > \text{O}$ , prepared by the action of acetic

acid and sodium acetate on trisdiketohydrindene, separates in golden-yellow scales, and does not melt at 320°.

T. M. L.

**Trisdihydroxybenzoylenebenzene.** By JOSEF LANDAU (*Ber.*, 1900, 33, 2440–2442).—The dark green substance (Abstr., 1898, i, 673) obtained from anhydrobisdiaethoxydiketohydrindene is better prepared by heating the sodium derivative of ethyl dimethoxydiketohydrindenecarboxylate,  $\text{C}_6\text{H}_2(\text{OMe})_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} > \text{CNa} \cdot \text{CO}_2\text{Et}$ , with fuming hydrochloric acid at 150°; it forms a very insoluble, black, granular powder, and has the formula  $(\text{C}_6\text{H}_4\text{O}_3)_x$ . Under similar conditions, anhydrobisketohydrindene is converted into tribenzoyl-

enebenzene, so that the dark green substance is probably *trisdi-hydroxybenzoylenebenzene*, and may be represented by the formula:



It forms a *hexabenzoyl* derivative when heated with benzoyl chloride at 150°.

C. F. B.

**2:2'-Dihydroxyflavone.** By STANISLAUS VON KOSTANECKI and A. SEIFART (*Ber.*, 1900, **33**, 2509—2512. Compare this vol., i, 448).—2:2'-*Diethoxyflavanone*,  $\text{C}_{15}\text{H}_{10}\text{O}_2(\text{OEt})_2$ , obtained by adding 50 per cent. sodium hydroxide solution to a hot alcoholic solution of 2-hydroxy-5-ethoxyacetophenone and *o*-ethoxybenzaldehyde, crystallises from alcohol in needles melting at 100—101°. It dissolves in concentrated sulphuric acid or alcoholic potassium hydroxide, yielding orange solutions; its alcoholic solution exhibits a blue fluorescence. The *monobromo*-derivative,  $\text{C}_{15}\text{H}_9\text{BrO}_2(\text{OEt})_2$ , crystallises in short needles, and melts at 101—102°.

2:2'-*Diethoxyflavone*,  $\text{C}_{15}\text{H}_8\text{O}_2(\text{OEt})_2$ , prepared by heating the preceding compound with alcoholic potassium hydroxide, crystallises in colourless needles melting at 106°; its solution in concentrated sulphuric acid is yellow with a green fluorescence.

The compound is hydrolysed by the action of sodium ethoxide, *o*-ethoxybenzoic acid and 2-hydroxy-5-ethoxyacetophenone resulting from the acidic fission, whilst the monoethyl ether of quinolcarboxylic acid is produced by the ketonic fission.

It was formerly stated that 3:2'-diethoxyflavone on hydrolysis yields salicylic acid, together with the monoethyl ether of resacetophenone (*Abstr.*, 1899, i, 524); in reality, the acidic fission gives rise to *o*-ethoxybenzoic acid. The product, which was taken to be salicylic acid, is the monoethyl ether of resorecylic acid, resulting from the ketonic fission.

2:2'-*Dihydroxyflavone*, produced by the action of hydrogen iodide on 2:2'-diethoxyflavone, is obtained in pale yellow needles melting at 304—305°; it dissolves in aqueous alkalis, yielding yellow solutions, and its solution in concentrated sulphuric acid is yellow with a green fluorescence. The *diacetyl* derivative forms colourless prisms and melts at 148—149°.

G. T. M.

**$\beta$ -Methyl-2-hydroxychromone.** By C. CRIVELLI and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, **33**, 2512—2513. Compare preceding abstract).—2:5-*Diethoxyacetylacetophenone*,  $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COMe}$ , obtained by mixing together 2:5-diethoxyacetophenone, ethyl acetate, and metallic sodium, acidifying with dilute acetic acid and extracting with ether, separates from dilute alcoholic solutions in colourless, flattened acicular crystals, and melts at 60°; its alcoholic solution is reddened by ferric chloride.

6-Hydroxy-2-methylchromone,  $\text{OH} \cdot \text{C}_6\text{H}_4 \begin{array}{c} \text{O} \text{---} \text{CMe} \\ | \\ \text{CO} \cdot \text{CH} \end{array}$ , produced from

the preceding compound by the prolonged action of hot hydriodic acid, crystallises in pale yellow prisms and melts at  $247^{\circ}$ ; it develops a yellow coloration when dissolved in alkalis; its solution in concentrated sulphuric acid is colourless with a greenish-blue fluorescence. The *acetyl* derivative crystallises in silky needles, and melts at  $99^{\circ}$ .

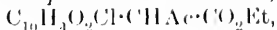
2:5-Diethoxybenzoylacetophenone,  $C_6H_3(OEt)_2 \cdot CO \cdot CH_2 \cdot CPh$ , prepared in a similar manner to the corresponding *acetyl* compound, crystallises in pale yellow, lustrous needles, and melts at  $72-74^{\circ}$ ; its alcoholic solution develops a red coloration with ferric chloride. When heated with hydriodic acid, it is converted into 2-hydroxyflavone (compare Abstr., 1899, i, 370). G. T. M.

4'-Hydroxyflavone. By S. GROSSMANN and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 2515—2517).—2:4'-Diethoxybenzoylacetophenone, prepared from ethyl 2-ethoxybenzoate and 4-ethoxyacetophenone by condensation with sodium (compare this vol., i, 239), crystallises from dilute alcohol in leaflets, and melts at  $110-111^{\circ}$ ; on boiling for several hours with hydriodic acid of sp. gr. 1.9, it yields 4'-hydroxyflavone,  $C_6H_4 \begin{array}{c} \diagup O-C_6H_4-OH \\ | \\ CO-CH \end{array}$ , which crystallises from pyridine-alcohol in small, white tufts of needles, melts at  $268^{\circ}$ , and dissolves in concentrated sulphuric acid giving a solution with an intense blue fluorescence. 4'-Acetoxyflavone crystallises from dilute alcohol in white needles and melts at  $137^{\circ}$ . 4'-Ethoxyflavone, obtained by warming 2:4'-diethoxybenzoylacetophenone for only a short time with hydriodic acid of sp. gr. 1.7, crystallises from alcohol in white needles melting at  $139-140^{\circ}$ . W. A. D.

2:3-Dichloro- $\alpha$ -naphthaquinolyl Derivatives of  $\beta$ -Diketones. By FR. MICHEL (*Ber.*, 1900, 33, 2402—2411. Compare Liebermann, this vol., i, 310).—Plagemann's dichloronaphthaquinone (Abstr., 1882, 973) is produced in small quantities in the preparation of 2:3-dichloro- $\alpha$ -naphthaquinone from the calcium derivative of dinitronaphthol; with ethyl sodiomalonate, it gives a diethyl chloronaphthaquinonemalonate,  $C_{10}H_4O_2Cl \cdot CH(CO_2Et)_2$ , which forms a yellow, crystalline powder, melts at  $86^{\circ}$ , and gives a blue coloration with sodium ethoxide.

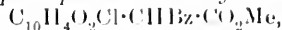
2-Chloro-3- $\alpha$ -cyanobenzyl- $\alpha$ -naphthaquinone,  $C_{10}H_4O_2Cl \cdot CHPh \cdot CN$ , prepared from 2:3-dichloro- $\alpha$ -naphthaquinone and the sodium derivative of benzyl cyanide, crystallises from alcohol in short, yellowish prisms, and melts at  $184^{\circ}$ .

Ethyl 2-chloro- $\alpha$ -naphthaquinone-3-acetoacetate,



prepared in a similar manner from ethyl sodioacetoacetate, separates from alcohol in yellow crystals and melts at  $106-107^{\circ}$ ; ethyl 2-acetonyl- $\alpha$ -naphthaquinone-3-acetate (Liebermann, *loc. cit.*), is produced as a by-product.

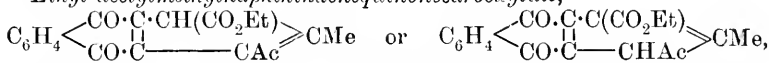
Methyl 2-chloro- $\alpha$ -naphthaquinone-3-benzoylacetate,



separates from methyl alcohol as a yellow, crystalline powder and melts at about  $172-173^{\circ}$ . 2-Chloro- $\alpha$ -naphthaquinone-3-acetylacetone,

$C_{10}H_4O_2Cl \cdot CHAc_2$ , crystallises from dilute alcohol in yellow scales and melts at  $131-132^\circ$ .

*Ethyl acetylmethylnaphthindenequinonecarboxylate*,



prepared by the action of sodioacetylacetone on ethyl chloro- $\alpha$ -naphthaquinoneacetoacetate, crystallises in minute, garnet-red needles and melts at  $177^\circ$ .

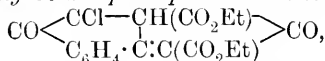
*2-Chloro- $\alpha$ -naphthaquinone-3-benzoylacetone*,  $C_{10}H_4O_2Cl \cdot CHAcBz$ , crystallises in large, yellow tablets from methyl alcohol and melts at  $109^\circ$ .

*Diethyl 2-chloro- $\alpha$ -naphthaquinone-3-oxalacetate*,



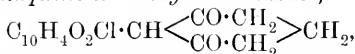
crystallises from alcohol in yellow, transparent prisms, melts at  $117-118^\circ$ , and loses carbon dioxide on further heating.

*Diethyl 2-chloroanhydrido- $\alpha$ -naphthaquinone-2-acetonedicarboxylate*,



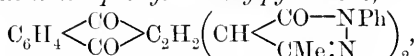
prepared by the action of diethyl sodioacetonedicarboxylate on dichloro- $\alpha$ -naphthaquinone, separates from alcohol as a dull yellow, crystalline powder and melts at  $159-160^\circ$ .

*2-Chloro- $\alpha$ -naphthaquinone-3-dihydroresorcinol*,



crystallises from alcohol in yellowish flakes melting at  $258^\circ$ .

*$\alpha$ -Naphthaquinonebis-1-phenyl-3-methylpyrazolone*,



prepared by the action of sodiophenylmethylpyrazolone, crystallises from alcohol in clear, blood-red, glistening flakes.

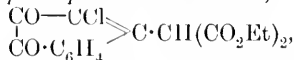
Measurements are given of the crystals of ethyl chloro- $\alpha$ -naphthaquinoneacetoacetate, chloro- $\alpha$ -naphthaquinonebenzoylacetone, and diethyl chloro- $\alpha$ -naphthaquinoneoxalacetate.

T. M. L.

**Halogen-substituted  $\beta$ -Naphthaquinolyl Derivatives of  $\beta$ -Diketones.** By H. HIRSCH (*Ber.*, 1900, **33**, 2412—2418. Compare preceding abstract).—*3-Chloro-2-bromo- $\beta$ -naphthaquinone*,  $C_6H_4 \begin{array}{c} \text{CO} \text{---} \text{CO} \\ \text{CBr} : \text{CCl} \end{array}$

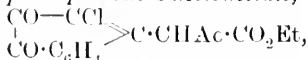
crystallises from acetic acid in bronze-coloured, glistening plates and melts at  $181.5^\circ$ ; with aniline, it gives Zincke and Fröhlich's 3-chloro-2-hydroxy- $\alpha$ -naphthaquinoneanilide (*Abstr.*, 1887, 54).

*Ethyl 3-chloro- $\beta$ -naphthaquinone-4-malonate*,



crystallises from alcohol in reddish-yellow prisms and melts at  $97^\circ$ .

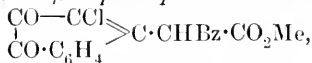
*Ethyl 3-chloro- $\beta$ -naphthaquinone-4-acetoacetate*,



crystallises from acetic acid in red, glistening needles and melts at

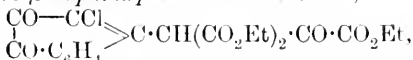
175°. 3-Chloro- $\beta$ -naphthaquinone-4-acetylacetone,  $\begin{array}{c} \text{CO}-\text{CCl} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHAc}_2$ , crystallises from acetic acid in red needles and melts at 218°.

3-Chloro- $\beta$ -naphthaquinone-4-benzoylacetone,  $\begin{array}{c} \text{CO}-\text{CCl} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHAcBz}$ , crystallises from acetic acid in dark-red, glistening tablets, and melts at 195°. Methyl 3-chloro- $\beta$ -naphthaquinone-4-benzoylacetate,



is a red, crystalline powder and melts at 173°.

Diethyl 3-chloro- $\beta$ -naphthaquinone-4-oxalacetate,

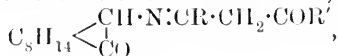


crystallises from alcohol in orange-red, glistening flakes, and melts at 127·5°.

3-Chloro- $\beta$ -naphthaquinone-4-deoxybenzoin,  $\begin{array}{c} \text{CO}-\text{CCl} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHPhBz}$ , forms glistening, golden-yellow, felted needles and melts at 195·5°.

3-Bromo- $\beta$ -naphthaquinone-4-acetylacetone,  $\begin{array}{c} \text{CO}-\text{CBr} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHAc}_2$ , forms deep-red needles and melts at 212°. T. M. L.

**Synthetical Bases of the Series of Terpenes and Camphors : Pyrrole Derivatives of the Camphor Group.** By PAUL DUDEN and W. TREFF (*Annalen*, 1900, 313, 25—58. Compare *Abstr.*, 1899, i, 779).—Aminocamphor undergoes condensation with aldehydes and  $\beta$ -ketones, yielding in the latter case a derivative,



which, under the influence of sodium ethoxide, becomes converted into an isomeric dicyclic compound,  $\text{C}_8\text{H}_{11} \begin{array}{c} \text{CH}\cdot\text{N}\cdot\text{CR} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \quad \text{CH}\cdot\text{COR}' \end{array}$ ; this readily loses water, changing into the pyrrole derivative,



The ring system,  $\begin{array}{c} \text{C} \quad \text{C} \quad \text{N} \quad \text{C} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \end{array}$  which forms the basis of these

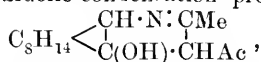
compounds, is entitled camphenepyrrole by the authors.

The pyrrole derivatives obtained in this way are distinguished as  $\alpha$ -compounds, because they undergo isomeric transformation when treated with mineral acids, yielding the so-called  $\beta$  compounds, which appear to be isopyrrole derivatives,  $\text{C}_8\text{H}_{11} \begin{array}{c} \text{C}\cdot\text{N}\cdot\text{CR} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{CH}\cdot\text{COR}' \end{array}$ , containing tertiary nitrogen.

[In part with D. HEYNSIUS.]—*Anhydroucetylacetoneaminocamphor*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{array}$ , prepared by merely mixing ethereal

solutions of acetylacetone and freshly prepared aminocamphor, crystallises from a mixture of ether and petroleum in long, colourless needles, and melts at  $88^{\circ}$ ; mineral acids resolve it into the components.

3-Acetyl-2-methylcamphenepyrrole ( $\alpha$ -derivative),  $C_8H_{14} \begin{smallmatrix} \diagup & \text{C} \cdot \text{NH} \cdot \text{CMe} \\ & | & | \\ & \text{C} & \text{---} & \text{CAc} \end{smallmatrix}$ , crystallises in colourless prisms melting at  $231^{\circ}$ , and in small quantities may be distilled at  $325^{\circ}$ ; it is obtained by recrystallising from glacial acetic acid the aldolic condensation product,

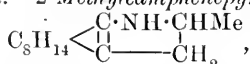


which results from anhydroacetylacetoneaminocamphor and sodium ethoxide, and crystallises from acetone, benzene, or alcohol in hexagonal leaflets melting at  $150^{\circ}$ . The acetyl derivative,  $C_{17}H_{23}O_2N$ , crystallises from methyl alcohol in long, slender needles melting at  $88^{\circ}$ , and the nitrosoamine,  $C_{15}H_{20}N_2O_3$ , separates from petroleum in yellowish prisms melting at  $119^{\circ}$ . Cinnamoylmethylcamphenepyrrole,

$C_8H_{14} \begin{smallmatrix} \diagup & \text{C} \cdot \text{NH} \cdot \text{CMe} \\ & | & | \\ & \text{C} & \text{---} & \text{C} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh} \end{smallmatrix}$ , produced by the action of benzaldehyde in presence of alkali, crystallises from a mixture of ether and petroleum in orange-yellow leaflets which melt to a reddish-brown liquid at  $180^{\circ}$ .

3-Acetyl-2-methylcamphenepyrrole ( $\beta$ -derivative),  $C_8H_{14} \begin{smallmatrix} \diagup & \text{C} \cdot \text{N} \cdot \text{CMe} \\ & | & | \\ & \text{C} & \text{---} & \text{CHAc} \end{smallmatrix}$ , formed when the  $\alpha$ -modification is heated with dilute mineral acids, crystallises from light petroleum in slender needles melting at  $134$ – $135^{\circ}$ ; it resists the action of reducing agents which attack the isomeride, and is also indifferent towards acetic anhydride.

3-Acetyl-2-methylcamphenepyrroline,  $C_8H_{14} \begin{smallmatrix} \diagup & \text{C} \cdot \text{NH} \cdot \text{CHMe} \\ & | & | \\ & \text{C} & \text{---} & \text{CHAc} \end{smallmatrix}$ , obtained by reducing  $\alpha$ -acetylmethylcamphenepyrrole with zinc dust and glacial acetic acid, is a colourless, alkaline, viscous oil which boils at  $226$ – $228^{\circ}$  under 120 mm. pressure, has a sp. gr. 1.0164 at  $9^{\circ}/4^{\circ}$ , and refractive index 1.5005 at  $9^{\circ}$ ; it has a camphor-like odour, and distils slowly in steam. The *picrate* crystallises in a network of small needles and melts at  $133$ – $134^{\circ}$ ; precipitates are formed with mercuric chloride, copper sulphate, and silver nitrate, but they are not characteristic. Oxidation by Tafel's method (Abstr., 1894, i, 301) regenerates acetylmethylcamphenepyrrole. 2-Methylcamphenepyrroline,

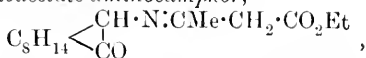


a bye-product in the formation of methylacetylcamphenepyrroline, boils at  $210$ – $212^{\circ}$  under 120 mm. pressure; the *picrate* melts at  $213^{\circ}$ .

When 3-acetyl-2-methylcamphenepyrroline is reduced with sodium amalgam in ice-cold dilute hydrochloric acid, 2-methyl-3-hydroxyethylcamphenepyrrolidine,  $C_8H_{14} \begin{smallmatrix} \diagup & \text{CH} \cdot \text{NH} \cdot \text{CHMe} \\ & | & | \\ & \text{CH} & \text{---} & \text{CH} \cdot \text{CHMe} \cdot \text{OH} \end{smallmatrix}$ , is produced in two modifications, of which the one more soluble in ether (A) crystallises from petroleum in highly refractive prisms melting at  $130$ – $131^{\circ}$ ,

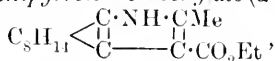
and forms the *picrate* and *platinichloride* melting and decomposing at 220—221° and 183—185° respectively; the isomeride (B), which is sparingly soluble in ether or petroleum, crystallises from alcohol in needles which melt at 222°, the *picrate* and *platinichloride* melting at 187° and 129—130° respectively, the latter decomposing.

*Anhydroethylacetouacetate-aminocamphor*,



obtained from ethyl acetoacetate and freshly prepared aminocamphor, crystallises from petroleum in long, colourless needles melting at 58°.

*Ethyl 2-methylcamphenepyrrole-3-carboxylate* ( $\alpha$ -derivative),

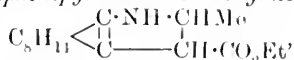


crystallises from ether or petroleum in colourless, rectangular leaflets, melts at 198°, and boils at 330°, slightly decomposing; the *acetyl* derivative,  $\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}$ , also forms colourless, rectangular leaflets, which melt at 63—64°, and the *nitrosoamine*,  $\text{C}_{16}\text{H}_{25}\text{O}_3\text{N}_2$ , separates from petroleum in small needles melting at 126—127°. The ester is somewhat indifferent towards hydrolytic agents, but alcoholic potash at 125° eliminates carbon dioxide, forming the *base*,  $\text{C}_{13}\text{H}_{21}\text{ON}$ , which melts at 136°, and yields the *picrate* melting at 141—142°. The

$\beta$ -derivative,  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{N} : \text{CMe} \\ \diagdown \text{C} \text{---} \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$ , crystallises from dilute alcohol in aggregates, and melts at 124—125°; it is hydrolysed by alcoholic potash, forming  $\beta$ -methylcamphenepyrrolecarboxylic acid,  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{N} : \text{CMe} \\ \diagdown \text{C} \text{---} \text{CH} \cdot \text{CO}_2\text{H} \end{array}$ , which darkens at 195°, melts, evolving gas, at 210°, and forms sodium, calcium, lead, copper, and silver salts which are not characteristic.

*2-Methylcamphenepyrrole*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{NH} \cdot \text{CMe} \\ \diagdown \text{C} \text{---} \text{CH} \end{array}$ , prepared by heating dried sodium  $\beta$ -methylcamphenepyrrolecarboxylate with lime, is a yellowish, viscous oil which crystallises in melting ice and boils at 220—224° under 210 mm. pressure.

*Ethyl 2-methylcamphenepyrroline-3-carboxylate*,



obtained by reducing ethyl methylcamphenepyrrolecarboxylate with zinc dust and acetic acid, boils at 245—246° under 207 mm. pressure and at 293—295° under atmospheric pressure; it is a strongly alkaline, viscous oil with an agreeable odour of peppermint.

*Anhydrobenzoylacetonecamincamphor*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{CH} \cdot \text{N} : \text{CMe} \cdot \text{CH}_2 \\ \diagdown \text{CO} \text{---} \text{COPh} \end{array}$ , crystallises from alcohol in long, colourless prisms, and melts at 111°; mineral acids resolve it into the components.

*3-Benzoyl-2-methylcamphenepyrrole*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{NH} \cdot \text{CMe} \\ \diagdown \text{C} \text{---} \text{C} \cdot \text{COPh} \end{array}$ , crystallises from benzene in pale yellow prisms and melts at 256°; the *acetyl* derivative crystallises from methyl alcohol in colourless prisms melting

at 104—105°, and the *phenylhydrazone* separates from benzene in leaflets melting at 132°. M. O. F.

**Synthetical Bases of the Series of Terpenes and Camphors : Camphenamine and  $\beta$ -isoCamphor.** By PAUL DUDEN and ALFRED E. MACINTYRE (*Annalen*, 1900, **313**, 59—79. Compare this vol., i, 302).—The authors have studied the action of nitrous acid on camphenamine,  $C_8H_{14} \begin{smallmatrix} C \cdot NH_2 \\ | \\ CH \end{smallmatrix}$ , expecting to obtain the enolic form of a ketone,  $C_{10}H_{16}O$ , which would differ from natural camphor in the mutual displacement of the carbonyl and methylene groups; the product, however, although having the anticipated empirical formula, is an unsaturated alcohol, and is quite indifferent towards hydroxylamine, semicarbazide, or sodium in alcohol. The name  $\beta$ -isocamphor is chosen by the authors for this compound.

[In part with J. ROBERTSON.]— $\beta$ -Aminoborneol,  $C_8H_{14} \begin{smallmatrix} CH \cdot NH_2 \\ | \\ CH \cdot OH \end{smallmatrix}$ , stereoisomeric with  $\alpha$ -aminoborneol (*Abstr.*, 1898, i, 677), and produced along with that substance when aminocamphor is reduced in boiling alcohol with excess of sodium, melts at 166° and boils at 262—263° under 751 mm. pressure; the specific rotatory power is  $[\alpha]_D - 42.46^\circ$  in methyl alcohol, that of the  $\alpha$ -modification being  $[\alpha]_D - 8.73^\circ$  in the same medium. The *aurichloride* forms slender needles melting at 227°; the *platinichloride* crystallises in leaflets melting at 293°; the *carbamide* melts at 211°, and the *acetyl* derivative at 130°. Attempts to withdraw the elements of water from aminoborneol by means of concentrated sulphuric acid, phosphoric oxide, phosphoric acid, concentrated hydrochloric acid, zinc chloride, and phosphorus pentasulphide have been unsuccessful. In order to arrive at camphenamine, therefore, it was necessary to convert aminoborneol first into chlorocamphanamine, and then eliminate hydrogen chloride from that compound (this vol., i, 302).

Chlorocamphanamine,  $C_8H_{14} \begin{smallmatrix} CH \cdot NH_2 \\ | \\ CHCl \end{smallmatrix}$ , is an oil which suddenly solidifies to the hydrochloride of camphenamine when an attempt is made to distil it; its *hydrochloride* crystallises in needles, and melts at 255°. The *platinichloride* decomposes above 260°, and the *picrate* melts at 190—191°.

Camphenamine,  $C_8H_{14} \begin{smallmatrix} C \cdot NH_2 \\ | \\ CH \end{smallmatrix}$ , is a colourless, mobile oil with a sweet, characteristic odour; it boils at 160—161° and at 205—207° under pressures of 200 mm. and 748 mm. respectively. It has a sp. gr. 0.9399 at 20°, and the refractive index 1.4935 at 20°; the specific rotatory power is  $[\alpha]_D - 4.15^\circ$  in methyl alcohol. The *hydrochloride*, *sulphate*, and *nitrate* decompose at 250°, 272°, and 198—199° respectively; the *platinichloride*, *aurichloride*, and *picrate* melt and decompose at 267—268°, 157—158°, and 214—215° respectively, whilst the *zinc double salt*,  $ZnSO_4(C_{10}H_{17}N)_2 \cdot H_2SO_4 \cdot 6H_2O$ , crystallises from water in lustrous leaflets and decomposes above 280°. The



*acetyl* derivative melts at  $100^{\circ}$ , and the *carbamide* separates from methyl alcohol in long prisms melting at  $190^{\circ}$ .

$\beta$ -iso*Camphor*,  $\text{OH} \cdot \text{C}_8\text{H}_{13} \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix}$ , prepared by the action of nitrous acid on camphenamine, sublimes in long needles having the odour and appearance of camphor, and melts at  $102^{\circ}$ ; the specific rotatory power is  $[\alpha]_D +17.65^{\circ}$  in methyl alcohol. The substance decolorises bromine in chloroform, combines with hydrogen bromide, and reduces alkaline permanganate. The *phenylurethane*,  $\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$ , crystallises from petroleum or dilute methyl alcohol in long needles melting at  $112^{\circ}$ .

M. O. F.

**Camphordioximes.** By FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 47—51).—By boiling bromopernitrosocamphor with excess of hydroxylamine hydrochloride and sodium hydroxide in dilute alcoholic solution, and then passing a current of carbon dioxide through the liquid, the camphor- $\beta$ -dioxime of Manasse is obtained; but when the hydroxylamine acts in the presence of sodium acetate, the products are the  $\alpha$ -dioxime and a new isomeride to which the name *camphor- $\delta$ -dioxime* is given. The latter is slightly soluble in alcohol, melts at about  $245^{\circ}$ , and gives a *dibenzoyl* derivative melting at  $188^{\circ}$ . The  $\alpha$ - and  $\delta$ -dioximes are also obtained when bromocamphor is boiled in aqueous alcoholic solution with hydroxylamine hydrochloride and sodium acetate. Four isomeric camphordioximes have now been prepared, this being the first instance in which all the isomeric dioximes of an asymmetrical diketone are known.

T. H. P.

**Fenchone.** By HANS CZERNY (*Ber.*, 1900, 33, 2287—2294).—*Bromofenchone*,  $\text{C}_{10}\text{H}_{15}\text{OBr}$ , obtained by heating fenchone with bromine for 20 hours at  $100^{\circ}$  in a sealed tube, is a colourless oil which boils at  $131\text{--}131^{\circ}$  under 18 mm. pressure, has a faint camphor-like odour, a sp. gr. 1.348 at  $12^{\circ}$ , a refractive index 1.51013, and a rotation  $+11.6^{\circ}$  in a 100 mm. tube. It is not readily volatile with steam, and yields neither an oxime nor a semicarbazone. When a solution in acetone is heated under pressure at  $130\text{--}140^{\circ}$  with freshly precipitated silver oxide, the substance is not attacked. If the compound is heated with zinc dust and acetic acid, fenchone is regenerated.

When bromofenchone is heated with excess of strong alcoholic potassium hydroxide, fencholenic acid is produced, identical with that obtained by Wallach (*Abstr.*, 1891, 219; 1892, 1237); it has a refractive index 1.4734 and sp. gr. 1.008 at  $22^{\circ}$ ; when cooled with liquid air, it crystallises. The acid dissolves easily in concentrated sulphuric acid, and if the solution is poured on ice, an isomeric compound,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , separates, which melts at  $77^{\circ}$  and crystallises from light petroleum in leaflets; it neither dissolves in solutions of sodium carbonate or hydroxide nor decolorises solutions of potassium permanganate.

*Tribromofenchane*,  $\text{C}_{10}\text{H}_7\text{Br}_3$ , formed by the gradual addition of bromine to a solution of fenchone in phosphorus trichloride, is a yellow oil which boils at  $181\text{--}186^{\circ}$  under 18 mm. pressure, and rapidly darkens in the air; it does not crystallise, but when cooled with

liquid air, solidifies to a vitreous mass. When tribromofenchane is boiled with zinc dust and acetic acid, it yields a crystalline *substance*,  $C_{10}H_{15}Br$ , which melts at  $115-116^{\circ}$ , has a camphor-like odour, sublimes very readily, decolorises solution of potassium permanganate, and in its general properties resembles the chlorofenchene of Gardner and Cockburn (Trans., 1897, 71, 1157; 1898, 73, 704).

E. G.

Carvotanacetone, Tanacetone, and Terpenone,  $C_{10}H_{16}O$ , (from Tetrahydrocarvone). By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 2454—2459).—Carvotanacetone is different from dihydrocarvone (compare Abstr., 1895, i, 675) and carvenone (Abstr., 1899, i, 225); from its direct reduction by sodium (to tetrahydrocarvone) the presence of a  $C:C:CO$  group may be inferred. When oxidised with dilute aqueous permanganate at  $0^{\circ}$ , it is now found to take up 60 per mol., and yield pyruvic and isopropylsuccinic acids; hence its formula must be  $CH_2 < \begin{smallmatrix} CHPr^{\beta} \cdot CH_2 \\ CH = CMe \end{smallmatrix} > CO$ , and it is an "ortho" derivative (this vol., i, 453). In harmony with this constitution is the fact that it unites with hydrogen sulphide in ammoniacal solution; the product melts at about  $95^{\circ}$ , and is probably identical with a substance obtained by Wallach and Schrader (Abstr., 1894, i, 537) from the high boiling fraction of thuja oil. In the conversion of tanacetone into carvotanacetone (Abstr., 1894, i, 339), it is thus the meta-bond of the former (this vol., i, 241) that disappears.

The existence of this meta-bond is maintained, as opposed to the para-bond assumed by Fromm (this vol., i, 402).

Von Baeyer's terpenone,  $C_{10}H_{16}O$ , yields an acid,  $C_9H_{16}O_4$ , when oxidised, and this yields isopropylsuccinic acid when further oxidised. Probably terpenone has the formula  $CH_2 < \begin{smallmatrix} CHPr^{\beta} - CH_2 \\ CH_2 \cdot C:(CH_2) \end{smallmatrix} > CO$ , and is the pseudo-form corresponding with carvotanacetone.

C. F. B.

Oil of Turpentine. By CHAS. T. TYRER and ALFRED WERTHEIMER (*Pharm. J.*, 1900, [iv], 11, 101—104).—Exhaustive fractionation of large quantities of American turpentine failed to show any optically inactive portion. About 0.5 per cent. boiling between  $160.2^{\circ}$  and  $160.4^{\circ}$  had a rotation of  $-0.04^{\circ}$  (measured in a 188.6 mm. tube); of 21 fractions the last eleven were levorotatory, the limit being  $-10.3^{\circ}$ .

R. L. J.

Viscosity of Essential Oils. By EDWIN DOWZARD (*Pharm. J.*, 1900, [iv], 11, 100).—The viscosity numbers of a series of oils as determined in a Reischauer viscometer, are: Lime, 177; bergamot, 219.8; orange, 112.5; citronella, 536; rosemary, 320; winter green, 261; sassafras, 238; lemon, 139.6. For citrene, the value is 106.8 and for a mixture of citrene and citral (7.5 per cent.) 114.9.

R. L. J.

Ethereal Oil of Fir Wood (*Pinus abies*, L.). By PETER KLASON (*Ber.*, 1900, 33, 2343—2344).—The wood of the fir-tree, employed in the preparation of sulphite cellulose, yields an oil which has been

usually regarded as oil of turpentine. An examination of this substance, however, has shown it to be cymene. M. O. F.

**Crystallised Constituent of the Essential Oil of Kaempferia Galanga, L.** By PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 38—41).—The rhizomes of *Kaempferia Galanga*, L., when distilled with steam, yield two volatile products, a light oil containing terpenoid substances and a heavy oil depositing crystals.

The crystalline product is ethyl *p*-methoxycinnamate, its properties corresponding exactly with those of the compound obtained from anisaldehyde and ethyl acetate (Vorländer, *Abstr.*, 1897, i, 275). The ester is readily hydrolysed by potassium hydroxide, and the corresponding acid is identical with the *p*-methoxycinnamic acid obtained by Knoevenagel (*Abstr.*, 1899, i, 145) from anisaldehyde and malonic acid; it melts at 169° to an opalescent liquid which becomes translucent at 185°. On reducing the substance in alcoholic solution with sodium amalgam, *p*-methoxypropionic acid is produced. G. T. M.

**German Rose Oil.** By HEINRICH WALBAUM and KARL STEPHAN (*Ber.*, 1900, 33, 2302—2308).—In addition to geraniol, always present in German rose oil (Bertram and Gildemeister, *Abstr.*, 1894, i, 253), the authors have found small quantities of normal *nonaldehyde* (which boils at 80—82° under 30 mm. pressure, has a density 0.8277 at 15°, and a molecular refraction  $n_D$  at 16° 1.42452) and of linalool, citral, phenyl-ethyl alcohol and citronellol. R. H. P.

**Constituents of East Indian Sandalwood Oil.** By HUGO VON SODEN (*Arch. Pharm.*, 1900, 238, 353—366. Compare *Abstr.*, 1899, i, 924, and Guerbet, this vol., i, 242, 401).—Santalol, known commercially as gonorol, is prepared from sandalwood oil by heating it with a little alcoholic potash, precipitating and washing the oil with water, and fractionating it under diminished pressure; the higher boiling part is santalol, and amounts to about 80 per cent. of the oil; the rest consists largely of sesquiterpenes. By repeated fractionation, conversion of appropriate fractions into santalylphthalic acids and regeneration of the santalol from these, an approximate separation into two substances was effected.  $\alpha$ -Santalol is probably a sesquiterpene alcohol,  $C_{15}H_{23}OH$ , and forms the chief constituent of "santalol" and East Indian sandalwood oil. It is a thick, colourless liquid with a faint odour of sandalwood, has a sp. gr. 0.977 at 15°, is feebly dextrorotatory, and boils at 301—302°, and 155° under pressures of 1 atm. and 8 mm. respectively;  $\alpha$ -santalyl acetate has a sp. gr. 0.988 at 15°, is dextrorotatory, and boils at 311—312°.  $\beta$ -Santalol, perhaps also  $C_{15}H_{21}O$ , has a rotation exceeding  $-45^\circ$ . C. F. B.

**East Indian Sandalwood Oil.** By FRIEDRICH MÜLLER (*Arch. Pharm.*, 1900, 238, 366—383).—The first fractions obtained in distilling East Indian sandalwood oil (from the wood of *Santalum album*, L.) were freed from acid by shaking with dilute aqueous sodium hydroxide, and then fractionated repeatedly under 15 mm. pressure; the fraction boiling above 135°, which consisted largely of sesquiterpenes, was neglected. Even then one fraction, boiling mostly at 126°, con-

sisted of a sesquiterpene; in addition, two other substances were isolated, and these are described below.

*Santene*,  $C_9H_{14}$ , a lower homologue of the terpenes, boils at  $35-37^\circ$  and  $139-140^\circ$  under 15 mm. and 1 atmo. pressure respectively, and has a sp. gr. 0.8710 at  $15^\circ$ . When treated in cooled acetic acid solution with ethyl nitrite and strong hydrochloric acid, it forms a blue, soluble *nitrosochloride* which melts and decomposes at  $108^\circ$ ; this changes gradually into a colourless modification (polymeride?), which at  $90^\circ$  is reconverted into the blue substance. No well characterised nitrolamine could be obtained, and although a crystalline, blue nitrosite was prepared, it seemed to be a mixture of two substances. By treatment with hydrogen chloride in ethereal solution an unstable *mono-hydrochloride*, melting at about  $80^\circ$ , was prepared. With bromine in chloroform solution, santene yields a *tribromide*,  $C_9H_{13}Br_3$ , which melts at  $62-63^\circ$ .

Another fraction consisted of two ketones which were separated by means of their semicarbazones. That one of which the *semicarbazone* is more soluble in alcohol and has the lower melting point,  $175^\circ$ , is present in the larger amount; it is named *santalone*,  $C_{11}H_{16}O$ . It boils at  $88-89^\circ$  and  $214-215^\circ$  under 15 mm. and 1 atmo. pressure respectively, has a sp. gr. 0.9906 at  $15^\circ$ , and a rotation  $-62^\circ$  in a 100 mm. tube; it forms an *oxime* which melts at  $74.5-75.5^\circ$ , and also a hydrobromide. The other ketone has not yet been investigated; its *semicarbazone* melts at  $224^\circ$ .

The acid obtained by shaking the first fractions of the sandalwood oil with aqueous sodium hydroxide, or the oil itself with aqueous sodium hydrogen carbonate, consists chiefly of *tere-santalic acid*,  $C_9H_{13}\cdot CO_2H$  (compare Guerbet, this vol., i, 242); its *silver* salt was analysed. In cooled methyl alcoholic solution, it combines with hydrogen chloride; the *hydrochloride* formed,  $C_9H_{14}Cl\cdot CO_2H$ , melts and decomposes at  $193^\circ$ . When shaken with cold dilute caustic soda, this hydrochloride forms a *lactone*,  $C_9H_{14}\begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix}$ , which melts at  $103^\circ$ ; when boiled with the

alkali, it forms, not an acid,  $OH\cdot C_9H_{14}\cdot CO_2H$ , but apparently an *oxy-hydroditeresantalic acid*,  $O(C_9H_{14}\cdot CO_2H)_2$ , which melts at  $143-144^\circ$ ; the *silver* salt of this acid was prepared and analysed. When a mixture of calcium teresantalate and acetate was distilled, a *hydrocarbon*,  $C_7H_{10}$ , boiling at  $105-110^\circ$ , and with a sp. gr. 0.818 at  $15^\circ$ , was obtained as the chief product. When teresantalic acid is boiled with dilute sulphuric acid, the chief product is a hydrocarbon,  $C_9H_{14}$ ,  *$\alpha$ -santene*, possibly identical with the santene previously described; it boils at  $140-142^\circ$ , has a sp. gr. 0.870 at  $15^\circ$ , and is inactive; its *tribromide* and *hydrochloride* melt at  $53-54^\circ$  and about  $65^\circ$  respectively. The alkaline liquid obtained by heating sandalwood oil with alcoholic potash (von Soden, preceding abstract) also contains teresantalic acid. This acid occurs in the oil to the extent of about 0.5 per cent., forming about half of the total acid present.

C. F. B.

The Balsam of *Abies canadensis* (Canada Balsam). By ALEXANDER TSCHIRCH and ED. BRÜNING (*Arch. Pharm.*, 1900, 238, 487-504).—From an ethereal solution of the balsam, dilute aqueous

ammonium carbonate extracts amorphous *canadic acid*,  $C_{19}H_{34}O_2$ ; this melts at  $135-136^\circ$  and neutralises  $1KOH$  as well in the cold as on boiling. Dilute aqueous sodium carbonate then extracts a mixture of acids; of these, amorphous  *$\alpha$ -canadinolic acid*,  $C_{19}H_{30}O_2$ , melting at  $89-95^\circ$ , is precipitated by alcoholic lead acetate, whilst an isomeric  *$\beta$  acid*, also amorphous and melting at  $90-95^\circ$ , remains in solution together with *canadolic acid*,  $C_{19}H_{28}O_2$ , which is crystalline and melts at  $143-145^\circ$ ; both canadinolic acids neutralise  $1KOH$  as well in the cold as on heating; canadolic acid neutralises  $1KOH$  in the cold, and nearly 2 on heating.

The residual ethereal solution is washed with aqueous potassium hydroxide, the ether distilled off, and the residue distilled with steam; an *etheral oil* distils over, boiling at  $160-167^\circ$ , whilst *canadoren*,  $C_{21}H_{40}O$ , remains behind; this is amorphous, melts at  $170^\circ$ , and is indifferent to alkalis. Some canadoren also separates in the solid state during the extraction of the original ethereal solution with sodium carbonate.

The balsam also contains an alkaloid soluble in water. In the dry distillation of the balsam, formic, acetic, and succinic acids are formed.

In 100 parts of the drug there are contained: canadic acid, 13; canadolic acid, 0.3;  $\alpha$ - and  $\beta$ -canadinolic acids ( $\alpha$  in much larger amount), 48-50; ethereal oil, 23-24; canadoren, 11-12; succinic acid, alkaloid, and impurities, 1-2.

The acids seem to contain no methoxyl groups. In contradistinction to the resen, the acids give the cholesterol reactions, including Tschugaeff's reaction (*Zeit. angew. Chem.*, 1900, No. 25), which is well fitted to distinguish between acids and resens. C. F. B.

**The Balsam of Abies Pectinata (Strasburg Turpentine).** By ALEXANDER TSCHIRCH and G. WEIGEL (*Arch. Pharm.*, 1900, 238, 411-427).—The investigation was conducted in a similar manner to that of larch turpentine (next abstract), and gave similar results. From the ethereal solution of the turpentine 1 per cent. ammonium carbonate solution extracted abienic acid; with 1 per cent. sodium carbonate solution, acids were extracted from the solution of which in alcohol abietolic acid crystallised whilst  $\alpha$ - and  $\beta$ -abietinolic acids remained dissolved; these could be separated by adding alcoholic lead acetate, which precipitated the  $\alpha$ -, but not the  $\beta$ -acid. The ethereal solution remaining, after removal of the ether, was distilled with steam, when an ethereal oil came over, whilst abietoresen remained behind.

*Abienic acid*,  $C_{13}H_{20}O_2$ , is an amorphous substance, and melts at  $114-115^\circ$ ; in the cold, it unites but slowly with enough  $N/2$  potassium hydroxide to form a monopotassium salt. *Abietolic acid*,  $C_{20}H_{28}O_2$ , is crystalline but rather unstable; it melts at  $145-153^\circ$ ; when titrated with  $N/2$  potassium hydroxide, it seems to form in the cold a monopotassium salt, and when heated a dipotassium salt.  $\alpha$ - and  $\beta$ -*Abietinolic acids* melt respectively at  $95-96^\circ$  and  $93-94^\circ$ ; both are amorphous, but have approximately the composition represented by  $C_{16}H_{24}O_2$ , and both seem to form monopotassium salts when titrated with  $N/2$  potassium hydroxide, but gradually take up still more potassium.

*Abietoresen*,  $C_{19}H_{13}O$ , is amorphous, melts at  $168-169^{\circ}$ , and is indifferent in its chemical character. The *etheral oil* boils for the most part at  $162-163^{\circ}$ , but higher boiling fractions are also present.

In 100 parts of the drug are contained: abienic acid, 8—10; abietolic acid, 1.5—2;  $\alpha$ - and  $\beta$ -abietinolic acids, 46—50; ethereal oil, readily volatile, 24—25, slightly volatile, 4—6; abietoresen, 12—16; alkaloid, colouring-matter, water, and impurities, 1—2; succinic acid, 0.05—0.08.

C. F. B.

The Balsam of *Larix Decidua* (Larch Turpentine). By ALEXANDER TSCHIRCH and G. WEIGEL (*Arch. Pharm.*, 1900, 238, 387—410).—This turpentine is collected chiefly in the Tyrol; the method adopted and the regulations in force are described at length. It was dissolved in ether, and the resin acids were extracted by repeated shaking with 1 per cent. aqueous sodium carbonate, finally with sodium hydroxide. The ether was then distilled off, and the residue distilled with steam, when an ethereal oil came over and an amorphous resen remained behind. Traces of succinic acid were obtained when the turpentine was submitted to dry distillation, and an alkaloidal substance was also present; esters were absent.

The resin acids were precipitated by acidifying the aqueous sodium carbonate solution, and dissolved in cold alcohol. When the solution was left for a time, *laricinolic acid*,  $C_{20}H_{30}O_2$ , melting at  $147-148^{\circ}$ , crystallised out. This reacts ordinarily as a monobasic acid; its *potassium, silver, calcium, and lead* salts were analysed. In the presence of excess of potassium hydroxide, it gradually takes up more potassium; when neutralised (to litmus paper) in alcoholic solution with alcoholic potash, it formed a salt,  $C_{20}H_{29}O_2K, 3C_{20}H_{30}O_2$ . It does not contain methoxyl, and it will not form either an ester or an acetyl derivative. The acids remaining in the alcoholic mother liquor were precipitated in part by alcoholic lead acetate, in part not. These two parts,  $\alpha$ - and  $\beta$ -*laricinolic acids* respectively, both have a composition corresponding with  $C_{18}H_{26}O_2$ , and are similar in their properties; they are perhaps identical. On titration with potassium hydroxide, they react as monobasic acids, but in the presence of excess of the alkali they take up more potassium. All these acids resemble the *cholesterols* in their colour reactions.

The *resen* could not be obtained in a form that invited investigation.

The *etheral oil* resembled oil of turpentine in general; it can be separated into two parts, boiling at about  $157^{\circ}$  and  $190^{\circ}$  respectively.

The drug contains the following amounts of the different constituents in 100 parts. *Laricinolic acid*, 4—5;  $\alpha$ - and  $\beta$ -*laricinolic acid*, 55—60; ethereal oil, readily volatile, 15—16, slightly volatile, 5—6; resen, 11—15; alkaloid, colouring-matter, and impurities, 2—4; succinic acid, 0.1—0.12.

C. F. B.

Plumieride and its Identity with Agoniadin. By ANTOINE P. N. FRANCHIMONT (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 35—38).—The author confirms his previous conclusions with regard to the identity of plumieride with ageniadin (*Abstr.*, 1899, i, 933), and proposes to retain the former term as the name of the substance.

G. T. M.

**Luteolin Methyl Ether as a Product of the Hydrolysis of a Glucoside from Parsley.** By EDUARD VONGERICHTEN (*Ber.*, 1900, 33, 2334—2342).—In addition to apiin, which, when hydrolysed, yields apigenin (A. G. Perkin, *Trans.*, 1897, 71, 805), and dextrose, parsley contains a second glucoside, which is probably oxyapiin methyl ether and, when hydrolysed, yields luteolin methyl ether and dextrose. *Luteolin methyl ether*,  $C_{16}H_{12}O_6$ , crystallises from alcohol in small needles melting at  $250^\circ$ , forms a *triacetyl* derivative, which crystallises in clusters of needles melting at  $195^\circ$ , a *tribenzoyl* derivative, which crystallises in slender needles melting at  $235^\circ$ , and can be easily converted into luteolin trimethyl ether (A. G. Perkin, *Trans.*, 1896, 69, 211, 799).  
R. H. P.

**The Fruits of Rhamnus Cathartica.** By ALEXANDER TSCHIRCH and R. POLACCO (*Arch. Pharm.*, 1900, 238, 459—477).—When the berries of *Rhamnus cathartica* are percolated with water, the percolate extracted with ether, and the substances so extracted crystallised from alcohol, *rhamnocitrin*,  $C_{13}H_{10}O_5$ , separates; this forms yellow crystals, fluoresces when dissolved in sulphuric acid, melts at  $221$ — $222^\circ$ , and forms a colourless *triacetyl* derivative melting at  $199$ — $200^\circ$ ; it is probably a trihydroxydihydrofluorone or dihydroxanthone. When the alcoholic extract is evaporated and the residue treated with toluene, *rhamnolutin*,  $C_{15}H_{10}O_6$ , remains undissolved (mixed with a little of a yellow substance,  $C_{11}H_{10}O_6$ ); it forms yellow crystals, fluoresces in sulphuric acid, melts above  $260^\circ$ , and forms a colourless *tetracetyl* derivative melting at  $182$ — $183^\circ$ ; it is possibly a tetrahydroxyflavone. In the toluene is dissolved a little *rhamnochrysin*,  $C_{13}H_{12}O_7$ , which forms orange-yellow crystals and melts at  $225$ — $226^\circ$ . In older berries, less rhamnocitrin and more rhamnochrysin is found. When the aqueous percolate, after extraction with ether, is hydrolysed with dilute sulphuric acid, ether then extracts  $\beta$ -*rhamnocitrin*,  $C_{13}H_{10}O_5$ , along with rhamnocitrin itself, which settles less rapidly from alcohol; the new substance melts above  $260^\circ$ , and forms a *diacetyl* derivative melting at  $190$ — $191^\circ$ .

When the berries, already exhausted with water, are percolated with 1 per cent. ammonia, the percolate acidified with hydrochloric acid, and the precipitate extracted with alcohol, a little emodin dissolves, and a nigrin, insoluble also in ether and acetone, remains. *Rhamno-emodin*,  $C_{15}H_{10}O_5$ , is orange-red, melts at  $251$ — $255^\circ$ , and resembles frangula-emodin greatly. *Rhamnonigrin* (C 56.3, H 5.3 per cent.) yields chrysamic acid when boiled with nitric acid; probably it was formed to a large extent from emodin compounds during the working up of the drug.

The purgative action is ascribed to the emodin. In addition to the substances enumerated, there are present an amorphous sugar, pectin, gummy substances, alkaloids, chlorophyll, fats, and a colouring-matter.

C. F. B.

**Senna.** By ALEXANDER TSCHIRCH and E. HIEPE (*Arch. Pharm.*, 1900, 238, 427—449).—From an aqueous percolate of senna leaves an unstable, yellowish, crystalline substance of the composition  $C_{14}H_{10}O_5$  was deposited. The percolate yielded an impure cathartic acid

when concentrated and mixed with alcohol; when hydrolysed with dilute sulphuric acid, it yielded yellow, unstable, crystalline *senna-rhamnetin*, which remains unmelted at  $260^{\circ}$ . A sample of cathartic acid obtained from Merck yielded senna-emodin and senna-chrysophanic acid when hydrolysed with boiling alcoholic potash.

A crude *anthraglucosennin* was obtained by percolating senna leaves with very dilute ammonia, and precipitating the extract with hydrochloric acid. It was extracted first with ether; when the substances extracted thereby are treated with toluene, there is left yellow, crystalline *glucosennin*,  $C_{22}H_{18}O_8$ , which remains unmelted at  $260^{\circ}$ , and reduces Fehling's solution only after hydrolysis with dilute sulphuric acid; from the toluene solution, light petroleum precipitates orange-red, crystalline *senna-emodin*,  $C_{15}H_{10}O_5$  (which melts at  $223-224^{\circ}$  and forms a yellow, crystalline *triacetyl* derivative melting at  $170^{\circ}$ ), whilst yellow, crystalline *sennachrysophanic acid*,  $C_{15}H_{10}O_4$ , melting at  $172^{\circ}$ , remains dissolved. (Senna-emodin appears to be identical with aloë-emodin, but different from rheum-emodin and frangula-emodin, which again are identical. Glucosennin is a derivative of hydroxymethylanthraquinone, and is probably an emodin-glucoside). After the extraction with ether was complete, acetone extracted amorphous, reddish-brown *sennaisoemodin*,  $C_{15}H_{10}O_5$ , soluble in light petroleum, together with senna-rhamnetin, which is insoluble in this solvent; there remained undissolved black, amorphous *sennanigrin* (C 60.5, H 5.0 per cent. approximately), which yields senna-emodin and sennachrysophanic acid when hydrolysed with boiling alcoholic potash, and chrysamic acid when boiled with nitric acid. It seems better to extract the leaves with 60 per cent. alcohol instead of with dilute ammonia.

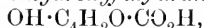
As the purgative action of the drug appears due to the hydroxymethylanthraquinone derivatives, the amount of these was estimated by a spectroscopic method; it was greatest in the fruits, but even then much less than in *Rheum* and *Frangula*; as regards the leaves, Alexandria senna contained the largest amount, Tinnevely the smallest.

C. F. B.

**Colouring Matter of Saffron.** By ALBERT HILGER (*Chem. Centr.*, 1900, ii, 576; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1899, 669).—The colouring matter of saffron is a phytostearyl ester of palmitic and stearic acids and contains also a hydrocarbon,  $C_nH_{2n+2}$ , which melts at  $71^{\circ}$ . In the living stigma, it is combined with glucose and an ethereal oil. The oil consists of terpene and a compound,  $C_{10}H_{18}O$ . The fractions of lower boiling points contain pinene and cineol.

E. W. W.

**Interaction of Furfuraldehyde and Caro's Reagent.** By CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Chem. News*, 1900, 82, 163).—With hydrogen peroxide, furfuraldehyde forms 3:2-hydroxyfurfuraldehyde and a small quantity of the corresponding acid (*Trans.*, 1899, 75, 749); with Caro's reagent, it yields what appears to be 5-hydroxyfurfuran-2-carboxylic acid,



which forms soluble lead and barium salts, gives a yellowish-red precipitate with ferric chloride like the isomeric pyromucic acid, is readily



hydrolysed, and when boiled in a solution kept at constant volume is decomposed yielding formic acid; hydrolysis also occurs on attempting to isolate the barium and calcium salts, with the production of a dibasic acid. By reduction with sodium amalgam, a hydroxyfurfuraldehyde is produced which differs from the others previously obtained.

Caro's reagent does not attack dextrin, but oxidises levulose slowly; it also oxidises the hydroxyfurfuraldehyde of the ligno-celluloses; hence it differs from the ordinary oxidising agents used in bleaching.

D. A. L.

**Composition of Berberine Phosphate.** By FRANK SHEDDEN (*Pharm. J.*, 1900, [iv], 11, 89—90).—Berberine phosphate,  $C_{20}H_{17}O_4N, 2H_3PO_4, 1\frac{1}{2}H_2O$ , prepared by adding excess of phosphoric acid to berberine-acetone, is a bright yellow, non-deliquescent crystalline substance soluble in 14.3 parts of water at 16°. The dehydrated salt dissolves in 15 parts of water at 15—16°. When prepared by Parsons and Wrampelmeier's method (*Proc. Amer. Pharm. Assoc.*, 1879, 514) it contains  $11H_2O$ .

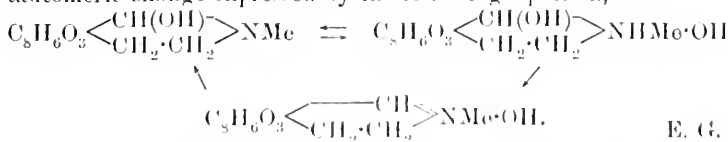
Estimation of berberine in its salts by conversion to the chloroform compound gives low results.

R. L. J.

**The Alkaloids of Ceanothus Americanus.** By HARRY M. GORDIN (*Pharm. Rev.*, 1900, 18, 266—268).—From an alcoholic solution of Gerlach's ceanothine (*Amer. J. Pharm.*, 63, 332) two fractions may be obtained, one of which melts at 255° and, like its picrate, dissolves sparingly in alcohol, the other melts at 200° and is easily soluble in alcohol, as also is its picrate.

R. L. J.

**Some Ammonium Compounds. VI. Formula of Cotarnine.** By HERMAN DECKER (*Ber.*, 1900, 33, 2273—2274).—Hantzsch and Kalb (this vol., i, 113) have suggested that solutions of cotarnine contain a compound,  $C_8H_6O_3 \begin{smallmatrix} \text{CH(OH)} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{NMe}$ , which they have termed pseudocotarnine. This formula was first proposed for cotarnine by the author (*J. pr. Chem.*, 1893, [ii], 47, 223), who considers that the abnormal conductivity of cotarnine solutions cannot be explained by the hypothesis of Hantzsch and Kalb, but is dependent on a tautomeric change expressed by the following equation,



E. G.

**Poisonous Boraginæ Alkaloids.** By KARL GREIMER (*Arch. Pharm.*, 1900, 238, 505—531).—*Cynoglossum offic.*, *Anchusa offic.*, and *Echium vulgare* contain an alkaloid, *cynoglossine*, of which the hydrochloride is crystalline and forms crystalline double compounds with mercuric chloride and platinum chloride (the latter in crystals of the regular system, with C 18.6, H 4.4, Pt 32.6); these were utilised in the purification of the alkaloid. The physiological action of cynoglossine is to paralyse the peripheral nerve terminations.

*Symphytum offic.* contains an alkaloid, *symphytocynoglossine*, which

in its chemical behaviour exhibits no difference from cynoglossine, but has a different physiological action; it paralyses the central nervous system.

In addition to cynoglossine and symphytocynoglossine the plants in question contain choline, which seems to be present in particularly large amount in the dried roots.

These four *Boraginæ* contain a glucoside, *consolidin*, which has also the properties of an alkaloid, and is decomposed by acids into glucose and consolicine. It paralyses the central nervous system.

*Consolicine*, the product of the decomposition of *consolidin*, is also an alkaloid, and is present as such in the four plants examined. It paralyses the central nervous system (with the exception, possibly, of the specimen from *Anchusa offic.*) and its action is three times as strong as that of *consolidin*. Its hydrochloride was obtained in the crystalline state.

C. F. B.

**Cytisine and some of its Alkyl Derivatives.** By A. RAUWERDA (*Arch. Pharm.*, 1900, 238, 477—486).—Cytisine was extracted from the seeds of *Cytisus laburnum*, L., by percolation with 80 per cent. alcohol and treatment of the extracted substance with chloroform, and was purified by distillation under 2 mm. pressure. It forms rhombic crystals [ $a:b:c=0.6768:1:0.5574$ ]. Methyleytisine crystallises from absolute alcohol in hemihedral rhombic needles [ $a:b:c=0.7973:1:0.9632$ ], from water with  $2H_2O$  in rhombic crystals [ $a:b:c=0.6156:1:1.8572$ ]. Determinations of the solubility and optical rotation of these two substances, in various solvents, are given. *Ethyleytisine* was only obtained as an oil. *Cetyleytisine* was obtained by heating powdered cytisine with cetyl iodide at  $100^\circ$ ; it melts at  $55-56^\circ$ , and has the specific rotation  $[\alpha]_D^{112}$  in chloroform and  $122^\circ 40'$  in methyl alcohol solution.

C. F. B.

**Damascenine, a Constituent of the Seeds of *Nigella Damascena*, L.** By HERBERT POMMERHNE (*Arch. Pharm.*, 1900, 238, 531—555. Compare Abstr., 1899, i, 964, and Schneider, *Pharm. Centralkh.*, 1890, 173).—The formula  $C_9H_{11}O_3N$  is now assigned to damascenine, from new analyses of the alkaloid and its salts; it contains only one and not two methoxyl groups. The following salts are described, with their formulae and melting points. ( $A=C_9H_{11}O_3N$ ).—Hydrochloride,  $A, HCl, H_2O$ ,  $194-197^\circ$ . Hydrobromide,  $A, HBr$ ,  $197-199^\circ$ ; with  $1H_2O$ ,  $117-118^\circ$ ; with  $2H_2O$ ,  $104-106^\circ$ . Hydroiodide,  $A, HI$ ,  $168-169^\circ$ ; with  $2H_2O$ ,  $112-115^\circ$ . Nitrate,  $A, HNO_3$ ,  $180^\circ$ ; with  $2H_2O$ ,  $93-95^\circ$ . Sulphates,  $2A, H_2SO_4$ ,  $183-185^\circ$ ;  $A, H_2SO_4$ ,  $203-205^\circ$ . Picrate,  $A, C_6H_3O_7N_3$ ,  $189-190^\circ$ . Platini-chloride,  $2A, H_2PtCl_6, 4H_2O$ ,  $197-198^\circ$ .

Damascenine, obtained from the hydrochloride by treatment with aqueous sodium carbonate and extraction with ether, melts at  $26^\circ$ . The yield is small, as a large part appears to undergo a molecular transformation, under the influence of the alkali, into a substance which is insoluble in ether, but forms salts identical, or nearly so, in composition and properties, with those of damascenine itself. Alcoholic potash effects the same transformation; the methoxyl group is not removed.

Damascenine unites with 1 mol. of methyl iodide in methyl alcoholic solution at  $100^{\circ}$ ; from the product several other salts were prepared. *Methiodide*,  $(A, Me)_2, 2H_2O$ ,  $168-170^{\circ}$ . *Methochloride platinichloride*,  $(A, Me)_2PtCl_6$ ,  $181-183^{\circ}$ ; *aurichloride*,  $(A, Me)AuCl_4$ ,  $153-155^{\circ}$ , *mercurichloride*,  $(A, Me)HgCl_2$ ,  $158-160^{\circ}$ . *Methonitrate*,  $120-121^{\circ}$ .  
C. F. B.

**Laudanosine.** By AMÉ PICTET and B. ATHANASESCU (*Ber.*, 1900, 33, 2346—2353).—Laudanosine, one of the more obscure opium alkaloids, is identical with *d*-*N*-methyltetrahydropapaverine, prepared by reducing papaverine methochloride and splitting the product with quinic acid; its constitution is therefore represented by the formula

$$\begin{array}{c} \text{OMe} \cdot \text{C} : \text{CH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe} \quad \text{CH} : \text{C}(\text{OMe}) \cdot \text{C} \cdot \text{OMe} \\ \text{OMe} \cdot \text{C} : \text{CH} \cdot \text{C} \quad \text{CH} \cdot \text{CH}_2 \cdot \text{C} : \text{CH} \end{array}$$

Racemic *N*-methyltetrahydropapaverine crystallises from dilute alcohol or light petroleum in long, white needles melting at  $115^{\circ}$ , and dissolves to some extent in boiling water; the alcoholic solution is strongly alkaline and has a bitter taste. With the usual reagents, the alkaloid develops colorations identical with those which characterise laudanosine. The *platinichloride*, *mercurichloride*, and *picrate* melt at  $160^{\circ}$ ,  $172^{\circ}$ , and  $174^{\circ}$  respectively; the *methiodide* and *ethiodide* form large crystals melting at  $215-217^{\circ}$  and  $202-203^{\circ}$  respectively. The base is more poisonous than papaverine, its toxic properties being comparable with those of thebaine; laudanosine also approaches thebaine in this respect, but unlike papaverine does not exert a narcotic effect.  
M. O. F.

**Inactive Nicotine.** By AMÉ PICTET and A. ROTSCHY (*Ber.*, 1900, 33, 2353—2355).—By heating aqueous solutions of nicotine monohydrochloride or sulphate in sealed tubes at  $180-250^{\circ}$  during periods varying according to the temperature and the nature of the salt, an inactive mixture of the antipodes has been obtained.  
M. O. F.

**Reduction of Nicotyrine to Inactive Nicotine.** By AMÉ PICTET (*Ber.*, 1900, 33, 2355—2356).—When dihydronicotyrine (*Abstr.*, 1898, i, 588), dissolved in glacial acetic acid is treated with bromine in the same solvent, a pale yellow, crystalline substance is produced which, on reduction with tin and hydrochloric acid, yields inactive nicotine.  
M. O. F.

**Pilocarpine.** By ADOLF PINNER and ERICH KOHLHAMMER (*Ber.*, 1900, 33, 2357—2363. Compare this vol., i, 456, and Jowett, *Trans.*, 1900, 77, 494, 851).—When pilocarpine is oxidised with potassium permanganate, all the nitrogen is eliminated, one half being converted into ammonia, the remainder disappearing in the form of methylamine; the dibasic acid,  $C_8H_{11}O_6$ , obtained in this way (compare, however, Jowett, *loc. cit.*, 855, and following abstract) is also produced when the alkaloid is oxidised with hydrogen peroxide. Chromic acid, however, gives rise to the dibasic acid,  $C_{11}H_{16}O_5N_2$ .

*Piluvic acid*,  $C_8H_{11}O_6$ , prepared by oxidising a 5 per cent. solution of pilocarpine with 0.5 per cent. potassium permanganate solution, yields the amorphous *silver* salt, which is very sensitive to light and

heat; the *potassium* salt is hygroscopic, and loses  $\text{H}_2\text{O}$  at  $100^\circ$ , yielding the *potassium* salt of the acid  $\text{C}_8\text{H}_{12}\text{O}_5$ , of which the *ethyl* ester boils at  $181$ – $183^\circ$  and  $293^\circ$  under pressures of 26 mm. and 755 mm. respectively. The *barium* salt,  $\text{C}_8\text{H}_{12}\text{O}_5\text{Ba}$ , is a white, amorphous powder, which loses no water at  $110^\circ$ , and only  $\frac{1}{2}\text{H}_2\text{O}$  at  $180^\circ$ .

*Pilocarpoeic acid*,  $\text{C}_{11}\text{H}_{16}\text{O}_5\text{N}_2$ , formed when pilocarpine dissolved in dilute sulphuric acid is oxidised with chromic acid, is a colourless gum, which melts below  $100^\circ$ , and dissolves very readily in water; the *barium* salt is amorphous, and only slightly hygroscopic.

M. O. F.

**Constitution of Pilocarpine.** By HOOPER A. D. JOWETT (*Ber.*, 1900, 33, 2892–2895. Compare preceding abstract).—Pinner and Kohlhammer's ethyl piluvate,  $\text{C}_8\text{H}_{10}\text{O}_5\text{Et}_2$ , boiling at  $293^\circ$ , is identical with the ester boiling at  $299^\circ$ , to which the author assigned the formula  $\text{C}_9\text{H}_{14}\text{O}_4$ . The accuracy of the latter formula, and of the view that the substance is the monoethyl ester of a monobasic lactonic acid is maintained.

T. M. L.

**The Alkaloids of Bocconia (Macleya) cordata.** By PAUL MURRILL and J. O. SCHLOTTERBECK (*Pharm. J.*, 1900, [iv], 11, 34–35; *Ber.*, 1900, 33, 2802–2807. Compare Eijkmann, *Abstr.*, 1885, 404; Hopfgartner, *Abstr.*, 1898, i, 606).—From *Bocconia cordata*, the tree celandine of the United States, the following alkaloids have been isolated. Protopine (macleiyne),  $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N}$ , forming about two-thirds of the alkaloidal yield, melting point  $208^\circ$  (corr.);  $\beta$ -homochelidonine,  $\text{C}_{21}\text{H}_{21}\text{O}_5\text{N}$ , forming about one-third of the yield, melting point  $158.5^\circ$  (corr.); and chelerythrine, which occurs only in very small quantity. The fluorescence of solutions of chelerythrine (compare Schmidt, Koenig and Tietz, *Abstr.*, 1893, i, 490), disappears with increased purity of the substance. Sanguinarine was not isolated, and was recognised only by the blood-red colour of its salts.

R. L. J.

**Syntheses in the Animal Organism. I. Piperidine Derivatives.** By HERMANN HILDEBRANDT (*Chem. Centr.*, 1900, ii, 202–203).—See this vol., ii, 676.

**Action of Bromoacetophenone on Piperidine.** By ERNST SCHMIDT and H. HARTONG VAN ARK (*Arch. Pharm.*, 1900, 238, 330–334).—When bromoacetone is allowed to remain with piperidine, best at the ordinary temperature and in ethereal solution, the *piperidylacetophenone bromide*,  $\text{CPhO}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}\cdot\text{HBr}$ , is obtained. This melts at  $220^\circ$ ; the corresponding *platinichloride* and *aurichloride* at  $204$ – $205^\circ$  and  $153$ – $154^\circ$  respectively. The base was isolated as an oily liquid; it forms a *methiodide*,  $\text{CPhO}\cdot\text{CH}_2\cdot\text{C}_5\text{H}_{10}\text{N}\cdot\text{MeI}$ , melting at  $185^\circ$ , from which an *aurichloride* and a *platinichloride*, melting respectively at  $129$ – $130^\circ$  and  $222^\circ$ , and a syrupy, alkaline hydroxide were prepared. The hydroxide was submitted to dry distillation, but only piperidine and methylpiperidine could be identified amongst the products.

The mother liquor from the piperidylacetophenone contains *piperidylacetophenone bromide*,  $\text{C}_5\text{NH}_{10}\text{Br}(\text{CH}_2\cdot\text{CPhO})_2\cdot\text{H}_2\text{O}$ ; this melts when anhydrous at  $164^\circ$ , the corresponding *platinichloride* at  $205^\circ$ .

C. F. B.

**Action of Cyanogen Bromide on Tertiary Amines. III.** By JULIUS VON BRAUN (*Ber.*, 1900, **33**, 2734—2736. Compare this vol., i, 641).—When cyanogen bromide reacts with methylpiperidine in ethereal solution, an unstable intermediate product is produced which decomposes into dimethylpiperidinium bromide and cyanopiperidine.

G. T. M.

**Thiazolines and Oxazolines.** By FRITZ SAULMANN (*Ber.*, 1900, **33**, 2634—2639. Compare Gabriel, *Abstr.*, 1890, 524; 1891, 701;

1892, 1331; 1897, i, 120).—2- $\beta$ -Naphthylthiazoline,  $\begin{array}{c} \text{CH}_2\text{-S} \\ | \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$ ,

obtained from  $\beta$ -naphthoylthiamide and ethylene bromide or bromoethylamine hydrobromide, is a colourless compound melting at  $80^\circ$  and readily soluble in the usual organic solvents. The *hydrobromide*,  $\text{C}_{13}\text{H}_{12}\text{NSBr}$ , has a pale yellow colour, melts at  $213^\circ$ , and is sparingly soluble in water; the *platinichloride* melts at  $218^\circ$ . 2- $\alpha$ -Naphthylthiazoline is an oil, the *picrate* of which forms yellow crystals melting at

$162^\circ$ . 2- $\alpha$ -Naphthyl-5-methylthiazoline,  $\begin{array}{c} \text{CHMe}\cdot\text{S} \\ | \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$ , obtained

from  $\alpha$ -naphthoylthiamide and  $\beta$ -bromopropylamine hydrobromide, is also an oil. 2- $\beta$ -Naphthylpenthiazoline,  $\text{CH}_2 \begin{array}{c} \text{CH}_2\text{-S} \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$ , obtained by the aid of trimethylene chlorobromide, melts at  $82^\circ$ , and its *picrate*, which is insoluble in water, at  $169^\circ$ . The isomeric  $\alpha$ -compound melts at  $103^\circ$ , and its *hydrochloride* decomposes at  $260^\circ$ .

*p*-Bromobenzoylthiamide, obtained from *p*-bromobenzonitrile and alcoholic ammonium sulphide, crystallises in yellow prisms melting at  $145^\circ$ , and when heated with ethylene bromide yields 2-*p*-bromophenylthiazoline, which crystallises in long needles melting at  $88^\circ$ ; the *picrate* melts at  $202^\circ$ , and the *platinichloride* decomposes at  $217^\circ$ . 2-*p*-Bromophenyl-5-methylthiazoline, is an oil, and its *picrate* melts at  $182^\circ$ .

$\beta$ -Naphthoylbromoethylamide,  $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_2\text{H}_4\text{Br}$ , crystallised from toluene, melts at  $152^\circ$ , and when treated with alcoholic

potash yields 2- $\beta$ -naphthylloxazoline,  $\begin{array}{c} \text{CH}_2\cdot\text{O} \\ | \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$ , as an oil.

$\alpha$ -Naphthoylbromoethylamide melts at  $97^\circ$ , and 2- $\alpha$ -naphthylloxazoline at  $50^\circ$ ; the *dichromates* of both bases are unstable.  $\beta$ -Naphthoyl- $\beta$ -bromopropylamide is sparingly soluble in ether and yields 2- $\beta$ -naphthyl-5-methylloxazoline in the form of a syrup, the *picrate* of which melts at  $197^\circ$ , and the *platinichloride* at  $209^\circ$ .  $\alpha$ -Naphthoyl- $\beta$ -bromopropylamide crystallises in felted needles and melts at  $100^\circ$ ; 2- $\alpha$ -naphthyl-5-methylloxazoline is an oil which forms a *picrate* melting at  $170^\circ$  and a *platinichloride* melting at  $197^\circ$ .

J. J. S.

**Action of Bromoacetophenone on Pyridine.** By ERNST SCHMIDT and H. HARTONG VAN ARK (*Arch. Pharm.*, 1900, **238**, 321—330. Compare Rumpel, *Abstr.*, 1898, i, 246, &c.).—From pyridine acetophenone (pyridinephenacyl) bromide,  $\text{C}^6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br}$ , melting at

198°, the corresponding *chloride* (with  $1\text{H}_2\text{O}$ ) *platinichloride*, *aurichloride*, and *mercurichloride*,  $\text{C}_{13}\text{H}_{12}\text{ONCl}\cdot\text{HgCl}_2$ , were prepared; these melt at 196—198°, 229—231°, 174°, and 189° respectively. The bromide is hydrolysed to benzoic acid and methylpyridine by warming with 5 per cent. aqueous sodium carbonate; when reduced with zinc dust and hydrochloric acid, it yields pyridine and apparently acetophenone. The chloride forms an *oxime*,  $\text{NOH}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Cl}$ , melting at 210°, from which a *platinichloride* and an *aurichloride*, melting at 196—198° and 136° respectively were prepared. The oxime chloride is not affected by boiling with acetyl chloride or with acetic anhydride and anhydrous sodium acetate; when heated in the water-bath with acetyl or benzoyl chloride, or at 150° with fuming hydrochloric acid, it is hydrolysed to hydroxylamine and pyridineacetophenone chloride; when heated for a short time at 100° with strong sulphuric acid, it yields a substance,  $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ , apparently of the nature of a sulphonic acid, together with hydroxylamine and pyridineacetophenone sulphate; when allowed to remain with a mixture of phosphorus pentachloride and oxychloride, it forms a compound, possibly  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Cl}$ , of which the *aurichloride* and *platinichloride* melt at 180° and 210—213° respectively. Attempts to reduce the oxime chloride to an amine in dilute acetic acid solution with sodium amalgam were unsuccessful. C. F. B.

**Additive Compounds formed by Nitriles with Tripyridinechromium Trichloride: Dithiocyanodiethylenediaminechromium Salts.** By PAUL PFEIFFER (*Ber.*, 1900, 33, 2686—2691).—The *additive compound*,  $\text{Cr}_3(\text{C}_5\text{NH}_5)_3\text{Cl}_3\cdot 2\text{MeCN}$ , separates rapidly from a solution of tripyridinechromium trichloride in acetonitrile in bright-green, microscopic rhombic plates. With propionitrile, the *compound*  $\text{Cr}_3(\text{C}_5\text{NH}_5)_3\text{Cl}_3\cdot \text{EtCN}$  appears to be formed, the composition of which varies on keeping; with benzonitrile a similar compound is obtained. Attempts to obtain analogous derivatives from dipyridinecupric chloride,  $\text{Cu}(\text{C}_5\text{NH}_5)_2\text{Cl}_2$ , and dipyridinezinc chloride failed.

On heating triethylenediaminechromium thiocyanate (this vol., i, 559) at 120—130°, it loses 1 mol. of ethylenediamine and yields *dithiocyanodiethylenediaminechromium thiocyanate*  $[\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SCN})_2]\text{SCN}\cdot 2\text{H}_2\text{O}$ , which crystallises from water in long, flat, lustrous, orange-yellow needles, and forms acid salts with concentrated hydrochloric and hydrobromic acids. With warm dilute sulphuric acid, the *salt*  $[\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SCN})_2]\text{SO}_4\cdot 2\text{H}_2\text{O}$  is obtained in long, transparent, efflorescent, orange prisms. Since the foregoing thiocyanate gives a normal reaction with ferric salts and the derived sulphate fails to do so, the author assumes the existence of the radicle  $[\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SCN})_2]$  in the latter; the salts thus belong to the type  $(\text{MA}_4\text{X}_2)\text{X}$ , of Werner's classification of additive compounds of amines with metallic salts. W. A. D.

**Luminosity of 1-Ethyl-2-quinolone.** By HERMAN DECKER (*Ber.*, 1900, 33, 2277—2278).—When large crystals of ethylquinolone are crushed, they emit a bluish light similar to that of the electric spark;

this effect is not produced by any other of many quinolone derivatives examined. E. G.

**Some Ammonium Compounds. VII. The Nitration of Alkyl-Quinoline Salts.** By HERMAN DECKER (*Ber.*, 1900, **33**, 2275—2277).—When ethylquinoline nitrate is left for a few hours in the cold with excess of nitrosulphuric acid, and the nitroethylquinoline so formed is liberated with alkali and oxidised by means of potassium ferricyanide, 5-nitro-1-ethyl-2-quinolone is produced. This method for the preparation of nitro-2-quinolones is much simpler than that previously described by the author (*Abstr.*, 1892, 879). E. G.

**Transformations of Phthaliminoketones.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, **33**, 2630—2634. Compare this vol., i, 358).—Benzylphthalimide undergoes no transformation in the presence of sodium ethoxide, whereas acetylphthalimide and phenacylphthalimide are readily converted into isocarbostyryl derivatives. 3-Acetyl-4-hydroxyisocarbostyryl,  $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C(OH)} \text{:} \text{C} \text{Ac} \end{smallmatrix}$  crystallises in colourless needles melting at about  $270^\circ$ , yields a *phenylhydrazone* crystallising in lemon-yellow, six-sided plates and decomposing at  $250^\circ$ , and, when reduced with hydriodic acid and red phosphorus, yields isocarbostyryl; an isomeric *acetyl* derivative melting at  $207\text{--}208^\circ$  is obtained by the action of acetic anhydride on 4-hydroxyisocarbostyryl. 3-Benzoyl-4-hydroxyisocarbostyryl crystallises from alcohol in yellow, hair-like needles melting at  $196\text{--}198^\circ$ . J. J. S.

**Aminonaphthacridinium Compounds.** By FRITZ ULLMANN and E. NAEF (*Ber.*, 1900, **33**, 2470—2475).—The monoacetyl derivative of “aminomethylnaphthacridine” (this vol., i, 361, where also see footnote as to nomenclature) forms the yellow iodide of “3'-acetylaminio-2':10-dimethyl-1:2-naphthacridinium,” when it is heated at  $140\text{--}150^\circ$  with methyl iodide and chloroform. The methylation is more easily effected by dissolving the acridine in nitrobenzene, and adding freshly distilled dimethyl sulphate to the solution at  $150\text{--}160^\circ$ ; the *acridinium methyl sulphate*,  $C_{19}H_{16} \begin{smallmatrix} \text{CH} \text{---} \\ \text{N} \text{Me}(\text{MeSO}_4) \end{smallmatrix} \text{C}_6H_2\text{Me} \cdot \text{NHAc}$ , crystallises out at once as a yellow powder. The acetyl group can be removed by boiling with dilute hydrochloric acid; from the solution, potassium nitrate precipitates red “aminodimethylnaphthacridinium” *nitrate*, which melts and decomposes at  $286\text{--}290^\circ$ ; from a dilute boiling solution of the nitrate, potassium dichromate precipitates the red *dichromate*; when dimethyl sulphate is used, there is no need to employ the acetyl-amino-compound; the aminoacridine itself can be methylated directly, the acridinium methyl sulphate separating in red crystals.

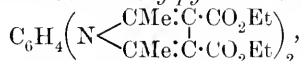
Ethyl bromide reacts with the acetyl-amino-compound rather less readily than methyl iodide does; the product, “3'-acetylaminio-2'-methyl-10-ethyl-1:2-naphthacridinium” *bromide*, forms yellow crystals and melts at  $265\text{--}269^\circ$ . The acetyl group can be removed by boiling with hydrobromic acid; the resulting “aminomethylethylnaphth-

*acridinium*" bromide forms red crystals, and melts and decomposes at 298°.

C. F. B.

**Difference of Basicity of the two Amino-groups of Substituted Diamines. I. *m*-Tolylenediamine.** By CARL BÜLOW (*Ber.*, 1900, 33, 2364—2370).—Tiemann observed (*Ber.*, 1870, 3, 221) that when *m*-tolylenediamine (1-methyl-2:4-diaminobenzene) is heated with slightly less than 2 mols. of glacial acetic acid and a very small quantity of water, it is the *p*-amino-group almost exclusively which is acetylated; similarly, Koch has shown (*Annalen*, 1870, 153, 132) that the diacetyl derivative is converted entirely into the 2-amino-4-acetamino-derivative when heated with 1 mol. of sodium hydroxide. The author finds that the same principle, namely, the greater reactivity of the 4-amino-group, underlies the condensation of *m*-tolylenediamine with ethyl diacetylsuccinate.

*Ethyl p*-phenylene-bis-2:5-dimethylpyrrole-3:4-dicarboxylate,



prepared by heating *p*-phenylenediamine with ethyl diacetylsuccinate in glacial acetic acid, crystallises from dilute alcohol in white scales melting at 172—173°.

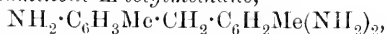
*Ethyl 1-o-acetylaminop-tolyl-2:5-dimethylpyrrole-3:4-dicarboxylate*,

$\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} \begin{array}{c} \text{CMe}:\text{C}:\text{CO}_2\text{Et} \\ \text{CMe}:\text{C}:\text{CO}_2\text{Et} \end{array}$ , obtained from *o*-acetyl-*m*-tolylene-

diamine and ethyl diacetylsuccinate, crystallises in white needles melting at 120—121°. *Ethyl 1-p-acetylaminoo-tolyl-2:5-dimethylpyrrole-3:4-dicarboxylate*,  $\text{C}_{21}\text{H}_{26}\text{O}_5\text{N}_2$ , prepared from *p*-acetyl-*m*-tolylenediamine and ethyl diacetosuccinate, melts at 160°. It is the former of these two substances which is produced on acetylating the condensation product of *m*-tolylenediamine and ethyldiacetosuccinate (*Annalen*, 1886, 236, 311.

M. O. F.

**Preparation of Diphenylmethane Derivatives from *p*- and *o*-Aminobenzylaniline and their Homologues.** By PAUL COHN and ARMIN FISCHER (*Ber.*, 1900, 33, 2586—2592).—The methods employed for the preparation of the compounds described in the paper have formed the subject of the German Patent, 107718, but the compounds themselves have not been described. 4-Aminophenyl-4-amino-*m*-tolylmethane,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , is formed by the action of hydrochloric acid on *o*-toluidine and *p*-aminobenzylaniline, and has already been described. 4-Aminophenyl-2:4-diamino-*m*-tolylmethane,  $\text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , is obtained in a similar manner from *m*-tolylenediamine, and forms compact, yellowish crystals melting at 139—140°. *p*-Amino-*m*-xylyl-*p*-toluidine forms white crystals melting at 93—94°, and with *m*-tolylenediamine yields 4:2':4'-triaminodi-*m*-tolylmethane,



which crystallises in slender, yellowish needles melting at 163°.

*p*-Dimethylaminobenzyl-*p*-toluidine,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , is obtained by the action of anhydroformaldehyde-*p*-toluidine on a mixture of dimethylaniline and *p*-toluidine, and melts at 105—106°;



the *hydrochloride*,  $C_{16}H_{20}N_2 \cdot 2HCl$ , crystallises in white needles. With aniline, the base yields 4-*amino-4'-dimethylaminodiphenylmethane*,  $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$ , which melts at  $90-91^\circ$ ; with *o*-toluidine, the same base yields 4-*dimethylaminophenyl-4-amino-m-tolylmethane*,  $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NH_2$ , which crystallises in greyish-white, silky needles, melts at  $92-93^\circ$ , and with *m*-tolylenediamine yields the corresponding 4-*dimethylaminophenyl-2':4'-diamino-m-tolylmethane*,  $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_2Me(NH_2)_2$ , which forms yellowish crystals and melts at  $112-113^\circ$ .

*p*-*Diethylaminobenzyl-p-toluidine*,  $NEt_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Me$ , crystallises in long, white prisms melting at  $59-60^\circ$ . *o*-*Amino-m-xylyl-p-toluidine*,  $NH_2 \cdot C_6H_3Me \cdot CH_2 \cdot NH \cdot C_6H_4Me$ , crystallises in white plates melting at  $87^\circ$ , and its *hydrochloride* in short prisms. With *m*-tolylenediamine it yields 2:2':4'-*triaminodi-m-tolylmethane*,  $NH_2 \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_2Me(NH_2)_2$ , melting at  $154^\circ$ . A. II.

**4-Hydroxypyrazole and its Derivatives.** By LUDWIG WOLFF (*Annalen*, 1900, **313**, 1-24).—The three methods by which the author has obtained derivatives of 4-hydroxypyrazole are the following: (1) Tetronic acid and benzenediazonium chloride yield the  $\alpha$ -phenyl-hydrazone of diketobutyrolactone (this vol., i, 584), which, when heated with sodium hydroxide, is transformed into 4-hydroxy-1-phenyl-

pyrazole-3-carboxylic acid,  $NPh \begin{smallmatrix} CH:C:OH \\ | \\ N=C \end{smallmatrix} CO_2H$ . (2) Ethyl  $\gamma$ -bromo-acetoacetate combines with benzenediazonium chloride, forming a phenylhydrazone which loses hydrogen bromide under the influence of alkalis, becoming converted into the ethyl salt of the foregoing acid. (3) Sodium diazotetronosulphonate (*loc. cit.*), under the influence of sodium hydroxide, followed by hydrochloric acid, yields 4-hydroxypyrazole-3-carboxylic acid.

[With A. LÜTTRINGHAUS].—4-*Hydroxypyrazole-3-carboxylic acid*,  $NH \begin{smallmatrix} CH:C:OH \\ | \\ N=C \end{smallmatrix} CO_2H$ , prepared by heating sodium diazotetronosulphonate with sodium hydroxide and adding cold dilute hydrochloric acid to the clear solution, crystallises from boiling water in aggregates of lustrous needles containing  $1H_2O$  and melting at  $204-205^\circ$  when carbon dioxide is eliminated; the aqueous solution develops a bluish-violet coloration with ferric chloride and becomes yellowish-red with sodium nitrite. The *tribenzoyl* derivative,  $C_{25}H_{16}O_6N_2$ , crystallises from alcohol in slender needles and melts at  $137^\circ$ ; the *benzoyl* derivative,  $C_{11}H_8O_4N_2$ , separates from dilute alcohol in aggregates and melts at  $210-212^\circ$ , evolving gas.

4-*Hydroxypyrazole*,  $NH \begin{smallmatrix} CH:C:OH \\ | \\ N=CH \end{smallmatrix}$ , obtained on eliminating carbon dioxide from the carboxylic acid, crystallises from chloroform in white plates and melts at  $118-118.5^\circ$ ; the aqueous solution, which is very feebly acidic, develops a greenish-blue coloration with ferric chloride, becomes yellowish-green with sodium nitrite, and reduces solutions of mercuric chloride and silver nitrate. The *picrate* forms long, yellow needles, and melts at  $128-129^\circ$ ; the *hydrochloride* melts at  $157^\circ$ , and the *platinichloride* dissolves very readily in water and in alcohol. The

*dibenzoyl* derivative,  $C_{17}H_{12}O_3N_2$ , crystallises from alcohol in long, white needles, and melts at  $109^\circ$ .

4-Hydroxy-1-methylpyrazole *methiodide*,  $C_5H_8ON_2I$ , prepared by heating 4-hydroxypyrazole with methyl iodide and methyl alcohol at  $120^\circ$ , crystallises from alcohol in plates melting at  $141^\circ$ ; the ammonium base crystallises in needles, which dissolve very readily in water, forming a strongly alkaline reducing solution, and the *platinichloride* crystallises in needles which decompose at  $212^\circ$ . 4-Hydroxy-1-methyl-

pyrazole,  $NMe \begin{smallmatrix} CH:C\cdot OH \\ \diagdown \quad | \\ N=C\cdot H \end{smallmatrix}$ , produced on heating the methiodide, crystallises from a mixture of chloroform and petroleum in white prisms and melts at  $89^\circ$ ; the hydrochloride is decomposed by water.

[With EDUARD FERTIG.]—The *a*-phenylhydrazone of ethyl  $\gamma$ -bromoacetoacetate,  $NHPh\cdot N:C(CO_2Et)\cdot CO\cdot CHBr$ , crystallises from dilute alcohol in yellow needles, and melts at  $80$ – $81^\circ$ ; it is sparingly soluble in sodium carbonate, but dissolves readily in sodium hydroxide.

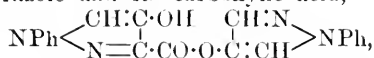
4-Hydroxy-1-phenylpyrazole-3-carboxylic acid,  $NPh \begin{smallmatrix} CH:C\cdot OH \\ \diagdown \quad | \\ N=C\cdot CO_2H \end{smallmatrix}$ , separates on adding hydrochloric acid to a solution of ethyl  $\gamma$ -bromoacetoacetate *a*-phenylhydrazone in hot sodium hydroxide, and crystallises from boiling water in needles which contain  $\frac{1}{2}H_2O$  and melt at  $130$ – $140^\circ$ ; the anhydrous compound crystallises from chloroform in large, lustrous prisms and melts at  $153$ – $154^\circ$ . The acid develops a deep blue coloration with aqueous ferric chloride, and becomes yellow or red with sodium nitrite and hydrochloric acid, even in dilute solutions. The *silver* salt crystallises in needles, and the *ethyl* ester forms colourless plates which melt at  $84$ – $45^\circ$ . The 5-phenylhydrazone of 1-phenyl-

4-keto-5-pyrazolone-3-carboxylic acid,  $NPh \begin{smallmatrix} C(:N\cdot NPh)\cdot CO \\ \diagdown \quad || \\ N= \quad C\cdot CO_2H \end{smallmatrix}$ , obtained on adding sodium phenylhydroxypyrazolecarboxylate to freshly diazotised aniline, crystallises from dilute acetic acid in lustrous red needles which melt and evolve gas at  $209^\circ$ . 5-iso-Nitroso-1-phenyl-

4-ketopyrazoline-3-carboxylic acid,  $NPh \begin{smallmatrix} C(:N\cdot OH)\cdot CO \\ \diagdown \quad || \\ N= \quad C\cdot CO_2H \end{smallmatrix}$ , formed on acidifying a solution of sodium phenylhydroxypyrazolecarboxylate and sodium nitrite, crystallises from dilute alcohol in bright red needles decomposing at  $190$ – $192^\circ$ .

4-Hydroxy-1-phenylpyrazole,  $NPh \begin{smallmatrix} CH:C\cdot OH \\ \diagdown \quad | \\ N=C\cdot H \end{smallmatrix}$ , produced on eliminating carbon dioxide from hydroxyphenylpyrazolecarboxylic acid, crystallises from very dilute alcohol in long, white needles, melts at  $119$ – $120^\circ$ , and boils at  $335^\circ$  under 736 mm. pressure, undergoing slight decomposition; it requires 570 parts of water at  $25^\circ$ , and 50–60 parts of boiling water to dissolve it, the aqueous solution becoming blue with ferric chloride and yellowish-red with sodium nitrite and acetic acid. The *hydrochloride* melts at  $80^\circ$  and loses hydrogen chloride in air; the *platinichloride* crystallises in orange-red prisms containing  $5H_2O$  and melts at about  $180^\circ$ , when it evolves gas. The *benzoyl* derivative,  $C_{16}H_{12}O_3N_2$ , crystallises in colourless plates and melts at  $78^\circ$ , and the *phenylurethane*,  $C_{16}H_{13}O_2N_3$ , separates from

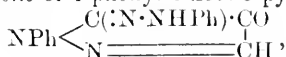
alcohol in long, white needles melting at  $168^{\circ}$ . The *anhydride* of phenylhydroxypyrazole and its carboxylic acid,



a bye-product in the preparation of hydroxyphenylpyrazole, crystallises from 80 per cent. alcohol in aggregates of lustrous needles melting at  $177^{\circ}$ ; it is neutral towards sodium carbonate, and is resolved by hot sodium hydroxide into hydroxyphenylpyrazole and its carboxylic acid.

*4-Chloro-1-phenylpyrazole*,  $\text{NPh} \left\langle \begin{array}{c} \text{CH:CCl} \\ \text{N}=\text{CH} \end{array} \right\rangle$ , obtained on heating the hydroxy-compound with phosphorus oxychloride at  $150^{\circ}$  during 10 hours (compare Michaelis and Röhmer, Abstr., 1899, i, 233), is identical with the compound prepared by Severini (Abstr., 1894, i, 145) from 1-phenylpyrazole and sodium hypochlorite; it crystallises in long, silky needles and melts at  $75-76^{\circ}$ .

The *5-phenylhydrazone* of 1-phenyl-4-keto-5-pyrazolone,



prepared by adding benzenediazonium chloride to the sodium derivative of hydroxyphenylpyrazole, crystallises from hot dilute acetic acid in lustrous, bronze-coloured needles melting at  $122-125^{\circ}$ . *5-iso-Nitroso-*

*1-phenyl-4-ketopyrazoline*,  $\text{NPh} \left\langle \begin{array}{c} \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \\ \text{N}=\text{CH} \end{array} \right\rangle$ , formed on adding acetic acid to a solution of hydroxyphenylpyrazole and sodium nitrite in dilute sodium hydroxide, crystallises from dilute alcohol in dark red prisms containing  $\text{H}_2\text{O}$ , and melts at  $119-120^{\circ}$ , slowly evolving gas.

*4-Hydroxy-1-phenylpyrazole methiodide*,  $\text{C}_{10}\text{H}_{11}\text{ON}_2\text{I}$ , crystallises from hot alcohol in long, white needles decomposing at  $195^{\circ}$ , when methyl iodide is eliminated; the ammonium *base*,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ , forms lustrous prisms which darken at  $120^{\circ}$  and melt at  $132-135^{\circ}$ . The *hydrochloride* crystallises in prisms decomposing at  $203^{\circ}$ , and the *platinichloride* forms yellow leaflets or prisms containing  $2\text{H}_2\text{O}$ , and melts, evolving gas, at  $193^{\circ}$ .  
M. O. F.

**5-Chloro- and 5-Bromo-1-phenyl 3-methylpyrazoles.** By AUGUST MICHAELIS and HEINRICH BEHN (*Ber.*, 1900, 33, 2595—2607. Compare Abstr., 1899, i, 233 and 941).—Phosphorus oxychloride and phenylmethylpyrazolone readily react when heated in a reflux apparatus, and the conversion of 5-chloro-1-phenyl-3-methylpyrazole into anti-pyrine takes place most readily in alcoholic solution.

When 5-chloro-1-phenyl-3-methylpyrazole is dissolved in fuming nitric acid, the product is a mixture of the mono- and di-nitro-derivatives, but with concentrated nitric acid (1 mol.) and sulphuric acid the mononitro-compound alone is formed. *5-Chloro-1-p-nitrophenyl-3-methylpyrazole* crystallises in long, thin needles melting at  $101^{\circ}$ , and is readily soluble in organic solvents and also in concentrated hydrochloric acid; when brominated in ethereal solution, it yields *5-chloro-4-bromo-1-p-nitrophenyl-3-methylpyrazole*, which crystallises in colourless

needles melting at  $152.5^{\circ}$ ; the same compound is obtained when 5-chloro-4-bromo-1-phenyl-3-methylpyrazole is nitrated, and hence the nitro-group must be in the benzene nucleus; that it occupies the *p*-position has been proved by direct synthesis from Altschul's *p*-nitrophenylmethylpyrazolone (Abstr., 1892, 1082) and phosphorus oxychloride. When heated at  $125^{\circ}$  for 6 hours with methyl iodide,

it yields the *methiodide*,  $\begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{CMe} \cdot \text{N}(\text{MeI}) \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , which crystallises in glistening, yellow plates melting and decomposing at  $229^{\circ}$ . 1-*m*-Nitrophenyl-3-methylpyrazolone, obtained by heating ethyl acetoacetate *m*-nitrophenylhydrazone (Abstr., 1890, 150) at  $140$ – $150^{\circ}$ , forms a yellow, crystalline powder insoluble in water or ether, and on treatment with phosphorus oxychloride is converted into 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole melting at  $103^{\circ}$  and yielding a *bromo*-derivative which melts at  $170^{\circ}$ . 1-*o*-Nitrophenyl-3-methylpyrazolone crystallises in orange-red needles melting at  $51^{\circ}$ , the corresponding 5-chloro-pyrazole melts at  $105.5^{\circ}$  and yields a *bromo*-derivative melting at  $123^{\circ}$ .

5-Chloro-1-*o*-*p*-dinitrophenyl-3-methylpyrazole crystallises from toluene in yellow needles, melts at  $181^{\circ}$ , and is insoluble in concentrated hydrochloric acid; when reduced and treated with nitrous acid, it yields a dye similar to Bismarck brown and with *p*-phenylenediamine it gives an intense tolylene-blue.

5-Chloro-1-*p*-aminophenyl-3-methylpyrazole crystallises from alcohol in glistening plates containing  $\text{1H}_2\text{O}$ ; it sinters at  $62^{\circ}$  and melts at  $76$ – $78^{\circ}$ ; its acetyl derivative,  $\begin{array}{c} \text{CH}:\text{CCl} \\ | \\ \text{CMe}=\text{N} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}, 2\text{H}_2\text{O}$ , loses its

water at  $80$ – $85^{\circ}$  and yields a *methiodide* melting at  $171^{\circ}$ . 5-Chloro-1-*p*-hydroxyphenyl-3-methylpyrazole crystallises from alcohol in glistening, yellow plates melting at  $145.5^{\circ}$ . 5-Bromo-1-phenyl-3-methylpyrazole, obtained by the action of phosphorus oxybromide at  $125^{\circ}$ , or of the tribromide at  $140$ – $150^{\circ}$ , on phenylmethylpyrazolone, is an oily liquid distilling at  $153^{\circ}$  under 15 mm., or at  $287^{\circ}$  under atmospheric pressure; it has a sp. gr. 1.4408 at  $8^{\circ}$ ; its *methiodide*,  $\text{C}_{10}\text{H}_6\text{N}_2\text{Br} \cdot \text{MeI}$ , forms colourless needles melting at  $233^{\circ}$ , and yields a *periodide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{BrI}_5$ , melting at  $57^{\circ}$ ; its *methobromide* melts and decomposes at  $218^{\circ}$ , and yields a *perbromide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Br}_4$ , melting at  $146^{\circ}$ ; the *methochloride* is very hygroscopic and melts at  $214^{\circ}$ . All three compounds, when treated with alcoholic potash or silver oxide, yield antipyrine. 4:5-Di-bromo-1-phenyl-3-methylpyrazole, obtained as a by-product in the preparation of the monobromo-compound, forms colourless, glistening plates melting at  $92^{\circ}$ , and is readily soluble in organic solvents or in concentrated hydrochloric acid.

5-Bromo-1-nitrophenyl-3-methylpyrazole crystallises in long needles, melts at  $104.5^{\circ}$  and is soluble in concentrated hydrochloric acid; the *dinitro*-derivative, which is insoluble in this acid, melts at  $185.5^{\circ}$ .

Both bromo- and chloro-phenylmethylpyrazoles, when reduced with zinc dust and hydrochloric acid, yield phenylmethylpyrazole melting at  $36.5^{\circ}$ , although with the chloro-compound the reduction is never complete. When phenylmethylpyrazole is brominated, the product is

4-bromo-1-phenyl-3-methylpyrazole, which is an oil distilling at 311—313° and having a sp. gr. 1·4575 at 8°; when further brominated, it yields the dibromo-derivative melting at 92°.

J. J. S.

**1-p-Bromophenyl-3-methyl-5-chloropyrazole.** By AUGUST MICHAELIS and G. SCHWABE (*Ber.*, 1900, 33, 2607—2614).—1-p-Bromophenyl-3-methylpyrazolone, obtained from p-bromophenyldiazine and ethyl acetoacetate, forms colourless crystals melting at 175°; it readily condenses with aldehydes, yielding sparingly soluble, coloured compounds; the 4-benzylidene compound crystallises in dark-red needles and melts at 142°, the 4-anisylidene derivative in orange-red crystals melting at 147°, and the 4-salicylidene compound in deep red needles melting at 196°.

5-Chloro-1-p-bromophenyl-3-methylpyrazole,  $\begin{array}{c} \text{CH:CCl} \\ | \\ \text{CMe:N} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$ , crystallises in long, colourless needles, melts at 82°, and distils at 165° under 11 mm. pressure; it dissolves in concentrated hydrochloric acid, yields a sparingly soluble but somewhat unstable *platinichloride*,  $(\text{C}_{10}\text{H}_8\text{N}_2\text{ClBr})_2 \cdot \text{H}_2\text{PtCl}_6$ , a *methiodide* decomposing and melting at 254°, and yielding a *picrate*,  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{ClBr} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , melting at 170°, a *methobromide* melting at 260°, and a *methochloride* melting at 228°.

Monobromoantipyrine,  $\begin{array}{c} \text{CH}=\text{C} \\ | \quad \text{O} < \\ \text{CMe}=\text{NMe} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$ , obtained by treating the methiodide, bromide, or chloride with alcoholic potash, crystallises from toluene or water in well-developed monoclinic prisms melting at 122° and boiling at 300° under 9 mm. pressure; it is readily soluble in most solvents and even dilute solutions exhibit the usual antipyrine reactions. Its *hydrochloride*,  $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br} \cdot \text{HCl}$ , melts and decomposes at 213°, its *platinichloride* at about 208—210°, and its *ferrocyanide*,  $(\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br})_2 \cdot \text{H}_4\text{FeC}_6\text{N}_6$ , forms a perfectly white precipitate which turns blue on exposure to the air.

5-Bromo-1-p-bromophenyl-3-methylpyrazole, obtained by the action of ethyl bromide on the chloro-derivative, crystallises in colourless needles melting at 87—88°, and yields a *methiodide* melting at 259°. 5-Chloro-4-bromo-1-bromophenyl-3-methylpyrazole, obtained when the chloro-derivative is treated with a solution of bromine in light petroleum, forms colourless needles melting at 143°. 4:5-Dibromo-1-bromophenyl-3-methylpyrazole melts at 150—151°, and the corresponding 4:5-dichloro-compound at 134·5°; the latter yields a *methiodide* melting and decomposing at 236°.

5-Chloro-1-bromonitrophenyl-3-methylpyrazole is formed when the chloropyrazole is treated with the theoretical amount of concentrated nitric acid in the presence of sulphuric acid; it crystallises in colourless needles, melts at 115°, and on reduction yields the *amino*-compound which melts at 99—100°. A *dinitro*-compound melting at 158° is formed when fuming nitric acid is employed.

1-Bromophenyl-3-methylpyrazole forms colourless crystals melting at 94°, and yielding a *methiodide* which melts at 224°; with bromine, it yields 4-bromo-1-bromophenyl-3-methylpyrazole melting at 98°.

J. J. S.

**5-Chloro-1-*p*-tolyl-3-methylpyrazole and Antipyrine-Bz\*-carb-  
oxylic Acid.** By AUGUST MICHAELIS and TH. SUDENDORF (*Ber.*, 1900,  
33, 2615—2622. Compare preceding abstracts).—5-Chloro-1-*p*-tolyl-  
3-methylpyrazole,  $C_{11}H_{11}N_2Cl$ , forms colourless crystals, melts at  $30^\circ$ ,  
distils at  $148^\circ$  under 12 mm., or at  $274^\circ$  under atmospheric pressure,  
dissolves in 20 per cent. hydrochloric acid and yields a *platinichloride*,  
 $(C_{11}H_{11}N_2Cl)_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , which crystallises in orange-coloured  
needles. The *methiodide*,  $C_{11}H_{11}N_2Cl, MeI$ , crystallises in needles melt-  
ing at  $245^\circ$  and yields a *picrate* melting at  $153^\circ$ . With ethyl iodide, the  
product is 5-iodo-1-*p*-tolyl-3-methylpyrazole *ethiodide*,  $C_{11}H_{11}N_2I, EtI$ ,  
melting at  $231^\circ$ . The *methobromide* melts at  $234^\circ$ , and the *methochloride*,  
 $C_{11}H_{11}N_2Cl, MeCl, H_2O$ , when dehydrated, melts at  $232^\circ$ . When these  
compounds are treated with alcoholic potash or moist silver oxide they  
yield *p*-tolylpyrine.

5-Chloro-4-bromo-1-*p*-tolyl-3-methylpyrazole crystallises in long needles,  
melts at  $66^\circ$ , and has a characteristic ethereal odour; the 4:5-dichloro-  
compound melts at  $57^\circ$ .

5-Chloro-1-nitrotolyl-3-methylpyrazole crystallises in colourless, glisten-  
ing needles, melts at  $81^\circ$ , and yields a *bromo-derivative* melting at  
 $136^\circ$ , identical with the compound obtained by nitrating 5-chloro-4-  
bromo-*p*-tolylmethylpyrazole. 5-Chloro-1-dinitro-*p*-tolyl-3-methylpyrazole  
melts at  $167^\circ$ . 1-*p*-Tolyl-3-methylpyrazole, obtained by reducing the  
chloropyrazole with hydriodic acid and red phosphorus, melts at  $50^\circ$ .

The most suitable oxidising agent for chlorotolylmethylpyrazoles is a  
sulphuric acid solution of chromium trioxide employed at tempera-  
tures below  $30^\circ$ . 5-Chloro-3-methylpyrazole-1-*p*-benzoic acid (5-chloro-  
1-phenyl-3-methylpyrazole-Bz-*p*-carboxylic acid)  $\begin{matrix} CH:CCl \\ CMe:N \end{matrix} > N \cdot C_6H_4 \cdot CO_2H$ ,

crystallises in felted needles melting at  $206$ — $208^\circ$  and is insoluble in  
water or ether, but soluble in hydrochloric acid; when heated with  
baryta, it yields chlorophenylmethylpyrazole, and thus its constitution  
is established. The *barium* salt (with  $3H_2O$ ) crystallises in needles,  
the *ethyl* ester is an oily liquid distilling at  $271^\circ$ , the *acid chloride*  
crystallises in needles melting at  $82^\circ$  and is readily decomposed by  
water, and the *anilide* crystallises in silky needles melting at  $163^\circ$ .  
When brominated, the acid yields 5-chloro-4-bromo-3-methylpyrazole-1-*p*-  
benzoic acid which crystallises in colourless needles melting and decom-  
posing at  $246^\circ$ ; the same product is also formed when chlorobromotolyl-  
methylpyrazole is oxidised with an aqueous acetic acid solution of  
chromic acid.

The *methiodide*,  $C_{11}H_9O_2N_2Cl, MeI$ , melts at  $264^\circ$ , and on treatment  
with alcoholic potash or moist silver oxide yields antipyrine-1-*p*-benzoic

acid (antipyrine-Bz-*p*-carboxylic acid,  $\begin{matrix} CH=C \\ | \quad O < \\ CMe= NMe \end{matrix} > N \cdot C_6H_4 \cdot CO_2H$ , to-

gether with chloromethylpyrazolebenzoic acid methochloride. The  
former crystallises from hot water in glistening plates melting at  $246^\circ$ ,  
and gives a faint red coloration with ferric chloride. J. J. S.

\* The authors use this symbol to indicate that the carboxylic group is attached to  
a carbon atom of the benzene ring.

**Aminomethylnaphthimidazolesulphonic Acid.** By ALFRED GALLINEK (*Ber.*, 1900, **33**, 2315—2317).—5-Amino-2-methyl- $\alpha$ -naphthimidazole, described by Meldola and Streatfeild (*Trans.*, 1887, **51**, 691) as unstable, can be prepared from dinitroacetophthalide, and when treated with fuming sulphuric acid yields a *monosulphonic* acid, which crystallises with  $H_2O$  in microscopic, lustrous, four-sided plates, forms characteristic *calcium*, *sodium*, and *barium* salts, and a *dialzo* compound, which when boiled with dilute sulphuric acid yields a *hydroxysulphonic* acid. The base, sulphonic acid, and hydroxysulphonic acid, when coupled with tetrazo-compounds, give dyes of black, deep-blue and blue tints respectively, and not red, as would be expected from derivatives of aminonaphthalene. R. H. P.

**Electrolytic Preparation of Benzidine.** By WALTHER LÖB (*Ber.*, 1900, **33**, 2329—2333. Compare *Abstr.*, 1898, i, 14).—A good yield (80 per cent.) of benzidine is obtained by the electrolysis of a solution of azobenzene in concentrated sulphuric acid at 20—30° with a current of cathode density 3—5 amperes per 1 sq. dem. with about 2.5—3 ampere-hours, a mercury cathode being used. Benzidine may be obtained (with a yield of 57—59 per cent. of the theoretical) directly by the electrolysis of nitrobenzene as follows: A 10 per cent. alcoholic solution of nitrobenzene containing 2 per cent. of sodium hydroxide is electrolysed in an earthenware cell with a current density of 3—5 amperes with 9 ampere-hours, a solution of sodium sulphate being used for the anode liquid; so soon as the whole is converted into azobenzene, the cathode liquid is strongly acidified with sulphuric acid dissolved in alcohol and again electrolysed, benzidine sulphate being precipitated as soon as it is formed. Nitrobenzene suspended in a weak alkaline solution can be similarly reduced to azoxybenzene, which, when electrolysed in acid solution, is reduced to benzidine. R. H. P.

**3-Phenylpurine.** By EMIL FISCHER and WOLF VON LOEBEN (*Ber.*, 1900, **33**, 2278—2281).—2:5:7-*Trichloro-3-phenylpurine*,  $N:CCl \cdot C \begin{array}{c} | \\ H \\ | \\ CCl:N \cdot C \cdot NPh \end{array} \gg CCl$ , obtained by heating dichloro-oxyphenylpurine with a mixture of phosphorus oxychloride and pentachloride in a sealed tube at 140° for 18 hours, melts at 210°—211°, and dissolves readily in hot acetic acid or chloroform, less easily in ether, and only very slightly in water; when quite pure it is colourless. It is easily soluble in concentrated sulphuric acid, and if the solution is heated for 15 minutes on the water-bath, hydrogen chloride is evolved, and dichloro-oxyphenylpurine produced.

When a solution of trichlorophenylpurine in alcohol (50 per cent.) is heated with zinc dust, *chloro-3-phenylpurine* separates in crystals; it melts at 162—163°, and dissolves easily in alcohol, less readily in ether or benzene, and is only slightly soluble in hot water. *Iodo-3-phenylpurine*, formed by the action of hydriodic acid on chlorophenylpurine, crystallises from hot alcohol in long, colourless needles, melts at 165—166°, and decomposes at a higher temperature with liberation of iodine; it is very slightly soluble in cold alcohol or hot water.

When iodophenylpurine is boiled with zinc-dust and water, *3-phenylpurine* is produced; it is obtained by sublimation under 5 mm. pressure

in colourless prismatic needles; it melts at 162—163°, is slightly soluble in boiling water, crystallises out in long needles, and is easily soluble in alcohol. The *hydrochloride*, *nitrate*, *platinichloride*, and *aurichloride* are described. E. G.

**Triazan Derivative from Nitrosoformylphenylhydrazine.** By ALFRED WOHL (*Ber.*, 1900, 33, 2759—2760).—*Nitrosoformylphenylhydrazine*,  $\text{NO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CHO}$ , obtained by the action of nitrous acid on formylphenylhydrazine, is an almost colourless substance which melts and decomposes at 84—85°, and dissolves readily in the ordinary organic solvents except light petroleum; it has acid properties and is soluble in dilute aqueous alkalis, from which it is precipitated by acids.

*Formylphenylbenzylidenetriazan*,  $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CHO}$ , prepared by reducing nitrosoformylphenylhydrazine in alcoholic solution with sodium amalgam and subsequent treatment with benzaldehyde, separates from benzene in crystals melting and decomposing at 182—183°; it has an acid character, being dissolved by dilute alkalis from which acids reprecipitate it unchanged. T. H. P.

**Benzylhydrazine.** By ALFRED WOHL and CARL OESTERLIN (*Ber.*, 1900, 33, 2736—2741).—*Benzylbenzylidenehydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$ , prepared by the partial reduction of benzalazine in alcoholic solution by means of sodium amalgam (2 atoms of sodium to 1 mol. of the azine), separates from its benzene solution on the addition of light petroleum in the form of white leaflets melting at 69—70° with evolution of nitrogen; it decomposes when kept with formation of benzaldehyde and on distillation gives rise to stilbene. *Acetylbenzylbenzylidenehydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{Ac}\cdot\text{N}\cdot\text{CHPh}$ , forms colourless, stable leaflets melting at 79°.

*Benzylhydrazine hydrochloride*, obtained together with benzaldehyde on heating benzylbenzylidenehydrazine with dilute hydrochloric acid, crystallises from alcohol in long, white, four-sided plates which melt at 110°. *Benzylhydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}_2$ , formed from the hydrochloride on distillation with lime, is a colourless, viscous liquid which is miscible with water, alcohol, or ether and boils at 103° under 41 mm. pressure; it undergoes gradual decomposition and on distillation under the ordinary pressure nitrogen is evolved and dibenzyl formed. On oxidation in acid solution by means of ferric chloride, it yields benzalazine and hydrazine, whilst the action of iodine in sodium carbonate solution gives benzyl iodide and nitrogen. *Nitrosobenzylhydrazine*,  $\text{C}_7\text{H}_7\cdot\text{N}_2\cdot\text{H}_2\cdot\text{NO}$ , is very stable and on crystallising from boiling water melts at 71°; its vapours have no unpleasant smell or poisonous action. By the action of dilute mineral acids, the nitroso-compound is converted into *benzylazoisimide*,  $\text{C}_7\text{H}_7\cdot\text{N}_3$ , a mobile oil which boils at 108° under 23 mm. pressure and explodes when strongly heated. T. H. P.

**Action of Nitrous Acid on Benzylhydrazine.** By THEODOR CURTIUS (*Ber.*, 1900, 33, 2561—2562).—*Nitrosobenzylhydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{NH}_2$ , obtained by the action of nitrous acid on benzylhydrazine hydrochloride, forms colourless leaflets or needles and melts at 70°; it crystallises unchanged from water, shows the Lieber-



mann reaction, and has strongly reducing properties. When mixed in aqueous solution with benzaldehyde, no action occurs, but on adding dilute sulphuric acid, nitrosobenzylbenzylidenehydrazone,  $\text{CH}_2\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{N}:\text{CHPh}$ , is formed.

*Benzylazoimide*,  $\text{CH}_2\text{Ph}\cdot\text{N}_3$ , obtained by warming nitrosobenzylhydrazine with dilute sulphuric acid, is a strongly refracting liquid which boils at  $85^\circ$  under 20 mm. pressure, is miscible with alcohol or ether, and has an odour recalling that of benzyl chloride; it is very stable towards hydrolytic agents.

*Nitroso-p-methylbenzylhydrazine*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{N}(\text{NO})\cdot\text{NH}_2$ , melts at  $78^\circ$ .  
W. A. D.

*as-Dibenzylhydrazines*. By MAX BUSCH and BRUNO WEISS (*Ber.* 1900, 33, 2701—2711. Compare *Abstr.* 1893, i, 419; 1898, i, 231).—*as-Dibenzylhydrazine* is best obtained by heating together hydrazine hydrate and benzyl chloride in dilute alcoholic solution.

*Dibenzylbenzylidenehydrazine*, formed as a bye-product in the preceding reaction, crystallises from alcohol in colourless needles or prisms and from petroleum in hexagonal plates; it melts at  $87^\circ$ . This substance is also obtained, together with benzylamine, by reducing dibenzylnitrosoamine with zinc dust and acetic acid.

*as-o-Dinitrodibenzylhydrazine*,  $\text{NH}_2\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , prepared by mixing together cold alcoholic solutions of hydrazine hydrate and *o*-nitrobenzyl chloride, crystallises from alcohol in yellow needles and melts at  $94$ – $95^\circ$ . Its *platinichloride* crystallises in yellow needles and melts at  $142^\circ$ .

*o-Trinitrotribenzylhydrazine*,  $\text{N}_2\text{H}(\text{CH}_2\cdot\text{C}_6\text{H}_3\cdot\text{NO}_2)_3$ , obtained as a bye-product in the preceding reaction, separates from a mixture of alcohol and chloroform in orange, prismatic crystals and melts at  $180$ – $181^\circ$ .

*o-Dinitrodibenzylnitrosoamine* melts at  $127^\circ$  and not at  $120^\circ$  as indicated by Gabriel and Jansen.

*Di-o-nitrodibenzylbenzylidenehydrazine*,  $\text{CHPh}:\text{N}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , produced by heating its generators on the water-bath, crystallises from alcohol in prisms and melts at  $115$ – $116^\circ$ .

*Formyldi-o-nitrodibenzylhydrazine*,  $(\text{CHO}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2)_2$ , prepared by heating di-*o*-nitrodibenzylhydrazine with formic acid, crystallises from dilute alcohol in colourless needles and melts at  $156^\circ$ . The *diacetyl* derivative, obtained in a similar manner by the use of acetic anhydride, forms yellow prisms and melts at  $125$ – $126^\circ$ .

*Acetyldi-o-aminodibenzylhydrazine*,  $\text{NHAc}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , is produced when di-*o*-nitrodibenzylhydrazine or di-*o*-nitrodibenzylnitrosoamine is reduced with zinc dust and acetic acid; it crystallises from benzene in colourless leaflets and melts at  $153$ – $154^\circ$ . It is distinctly basic, dissolving readily in dilute mineral acids; the hydrochloride and platinichloride could not, however, be obtained crystalline. A *triacetyl* derivative results from the action of acetic anhydride on the preceding compound; this substance crystallises from alcohol and petroleum in colourless leaflets, melts at  $239^\circ$ , and is devoid of basic properties.

*as-Di-p-nitrodibenzylhydrazine*,  $\text{NH}_2\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , prepared in

a similar manner to its ortho-isomeride, crystallises from alcohol in aggregates of needles melting at  $137^{\circ}$ — $180^{\circ}$ ; the *hydrochloride* crystallises in needles and melts at  $242^{\circ}$ .

*Di-p-nitrodibenzylbenzylidenehydrazine* forms yellow prisms and melts at  $170^{\circ}$ .

When *as*-dibenzylhydrazine is oxidised in alcoholic solution with mercuric oxide, the whole of its nitrogen is quantitatively liberated and dibenzyl is produced. *as*-Di-*o*-nitrodibenzylhydrazine and its para-isomeride undergo a similar change, and the corresponding dinitrodibenzyls are obtained.

*Di-o-nitrodibenzylsemicarbazide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , produced by heating an alcoholic solution of *o*-nitrobenzyl chloride and semicarbazide for 12 hours at  $100^{\circ}$ , is insoluble in the ordinary solvents and separates from glacial acetic acid in colourless prisms melting at  $234^{\circ}$ .

G. T. M.

**Reduction of Benzylidenehydrazine to Benzylhydrazine.** By THEODOR CURTIUS (*Ber.*, 1900, 33, 2459—2460).—This reduction, which is otherwise difficult to accomplish, may be effected by shaking a solution of benzylidenehydrazine in absolute alcohol with 4 per cent. sodium amalgam at the ordinary temperature. The solution is then mixed with water and dilute hydrochloric acid, filtered from benzaldazine, and evaporated to dryness; the benzylhydrazine hydrochloride is extracted with hot absolute alcohol from the residue, which in addition contains the hydrochlorides of benzylamine and hydrazine.

C. F. B.

**Nitrobenzylidenehydrazines.** By THEODOR CURTIUS and A. LUBLIN (*Ber.*, 1900, 33, 2460—2466).—The nitrobenzylidenehydrazines,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NH}_2$ , unlike benzylidenehydrazine itself, are comparatively stable substances, although they undergo transformation in moist air, probably into the tetrazones first and the aldazines finally. They are prepared by gradually adding alcoholic solutions of the nitrobenzaldehydes to a considerable excess of hydrazine hydrate. When oxidised in benzene solution with mercuric oxide, they form tetrazones,  $\text{N}_2(\text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , which readily lose nitrogen forming aldazines,  $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ . When treated in alcoholic solution with acids they yield aldazines and hydrazine salts. They condense with aldehydes,  $\text{R} \cdot \text{CHO}$ , and ketones,  $\text{CR}_2\text{O}$ , to form mixed aldazines,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{N} : \text{CHR}$ , and aldoketazines,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{N} : \text{CR}_2$ , respectively. The compounds prepared are enumerated below with their melting points.

*Nitrobenzylidenehydrazines*: *m*-, yellow,  $107^{\circ}$ ; *o*-, yellow,  $76^{\circ}$ ; *p*-, orange-yellow,  $134^{\circ}$ , more stable than the others. *Dinitrobenzylidenetetrazones*: all reddish-brown and gummy. *Nitrobenzaldazines*: *m*-, yellowish,  $194^{\circ}$ ; *o*-,  $182^{\circ}$  (apparently not new); *p*-, yellowish,  $296^{\circ}$ . *Nitrobenzalacetaldazines*: *m*-, grey,  $68^{\circ}$ ; *o*-, red, decomposes before melting; *p*-, yellowish-grey,  $140^{\circ}$ , with decomposition. *Nitrobenzalbenzaldazines*: *m*-, yellow,  $125^{\circ}$ ; *o*-, yellow,  $105^{\circ}$ ; *p*-, yellow,  $256^{\circ}$ . *m*-Nitrobenzal-*o*-hydroxybenzaldazine: *m*-, yellow,  $162^{\circ}$ . *p*-Nitrobenzalcinnaaldazine, yellow,  $169^{\circ}$ . *Nitrobenzalacetonzazine*: *m*-, colourless,  $91^{\circ}$ ; *o*-, yellowish-white,  $70^{\circ}$ ; *p*-, yellow,  $88^{\circ}$ .

C. F. B.

**Preparation of Aromatic Aldehydes from the Corresponding Acids by Means of Hydrazine.** By THEODOR CURTIUS (*Ber.*, 1900, 33, 2559—2561).—The product obtained by Davidis (*Abstr.*, 1897, i, 5) on heating dextrose with benzoylhydrazine and dilute aqueous sodium hydroxide, and thought to be a dextrose benzosazone, has been shown by Pinkus (*Abstr.*, 1898, i, 224) to consist of a mixture of the benzosazones of glyoxal and methylglyoxal; at the ordinary temperature, however, the dextrose does not enter into action, *benzoylbenzylidenehydrazone*,  $C_6H_5 \cdot CH:N \cdot NH \cdot Bz$ , being formed, owing to partial hydrolysis of the benzoylhydrazine occurring, accompanied by reduction of the benzoic acid to benzaldehyde by the hydrazine thus liberated. The product is sparingly soluble in all solvents, melts at  $204-205^\circ$ , and is easily hydrolysed by boiling dilute sulphuric acid to benzoic acid, benzaldehyde, and hydrazine.

[With H. MELSBACH.]—The conditions necessary to transform a large number of aromatic hydrazides into the corresponding tertiary hydrazones,  $R \cdot CO \cdot NH \cdot N : CHR$ , have been investigated; on distilling these with dilute sulphuric acid, the corresponding aldehydes are easily isolated. In addition, it is shown that the ultimate product of the action of aqueous alkalis on aromatic hydrazines are aldazines of the type  $CHPh : N : N : CHPh$ .

W. A. D.

**Tinctorial Properties of Diphenylcarbazone.** By PAUL CAZENÈVE and PAUL SISLEY (*Bull. Soc. Chim.*, 1900, [iii], 23, 769—771).—Diphenylcarbazone,  $NHPh \cdot NH \cdot CO \cdot N : NPh$ , resembles other colouring matters in its asymmetric character, but differs from them in containing the special auxochrome group,  $CO \cdot NH$ , which exhibits acid properties. Hence it dyes silk and wool directly, but the tint produced is fugitive and destroyed by dilute mineral acids. When metallic salts are used as mordants, more or less unstable tints ranging from rose to violet are produced, the brightest and most resistant being obtained with mercuric nitrate.

N. L.

**Influence of the Orientation of Chromophores on the Colour and other Properties of Dyes.** By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1900, 33, 2497—2503).—The azo-dyes derived from the nitro- and chloro-toluidines and 1-naphthol-4-sulphonic acid have been studied with a view of establishing a relationship between the colour of the compound and the orientation of its chromophores.

The bases obtained by nitrating aceto-*o*-toluidide and hydrolysing the crude product of nitration are most conveniently separated by distilling the solution of their hydrochlorides in steam, 3-nitro-2-toluidine passing over into the distillate whilst 5-nitro-2-toluidine remains in the residue.

In preparing 5-chloro-2-acetotoluidide, it is better to employ sodium chlorate and hydrochloric acid rather than free chlorine.

The azo-derivatives of the nitrotoluidines containing their nitro-radicles in the ortho- or meta-position relatively to the azo-group give practically the same shade of orange when dyed on wool from a dilute sulphuric acid bath. The colouring matter from 3-nitro-2-toluidine which contains a nitro-group in the para-position to the other chromophore is distinctly redder in colour. These compounds differ from one

another in their stability to light; the presence of a nitro-group in the ortho-position relatively to the azo-chromophore render the dyes more fugitive, that derived from the consecutive base 3-nitro-2-toluidine being the most sensitive of all.

The azo-compounds of 4:2- and 5:2-chlorotoluidines give redder shades than the corresponding derivatives of the chlorinated *m*- and *p*-toluidines but the consecutive base 6-chloro-2-toluidine yields the deepest yellow colouring matter.

Those azo-derivatives of the chlorotoluidines containing chlorine atoms in the ortho-position to the azo-groups are more fugitive than their meta- and para-isomerides; the consecutive arrangement of the three substituent radicles also diminishes the stability towards light.

There is no simple relationship between the solubility of these colouring matters and their constitution. G. T. M.

**Action of Hypochlorous Acid on Primary Aromatic Amines.** By WILHELM MEIGEN and W. NORMANN (*Ber.*, 1900, 33, 2711—2717).—Although the process described by Claus and Jaeck in the D. R. P. No. 78748, is stated to be a general method for preparing azines by the action of hypochlorous acid on primary aromatic amines, yet this result is attained only in the case of  $\beta$ -naphthylamine and certain of its derivatives;  $\alpha$ -naphthylamine and its sulphonic acids do not yield definite products; aniline and its homologues and their bromo-, nitro-, and sulpho-derivatives give rise to azo-compounds, and only from 2-nitro-*p*-toluidine is a small amount of a bye-product obtained, which is probably a nitrotolazine.

The aromatic base, dissolved in benzene, is shaken up with excess of the sodium hypochlorite solution, the product being obtained in a crystalline form on concentrating the solution of the hydrocarbon.

*o*-Dinitroazobenzene, obtained from *o*-nitroaniline, crystallises in straw-yellow, felted needles and melts at 194—195°. Corresponding azo-compounds are produced from the *m*- and *p*-nitroanilines; *m*-dinitroazobenzene agreeing in its properties with the substance described by Werner and Stiasny (this vol., i, 194).

2:2'-Dinitro-4:4'-azotoluene, prepared from 2-nitro-*p*-toluidine, crystallises in red leaflets and melts at 149°.

Sodium-1:2-naphthazine-6:6'-disulphonate, obtained by treating 2-naphthylamine-6-sulphonic acid with hypochlorous acid, forms a crystalline, greenish-yellow powder, which is soluble in water. Like  $\alpha\beta$ -naphthazine, it develops a violet coloration with concentrated sulphuric acid. The sulphonic groups are not removed by heating with mineral acids, but the unsulphonated azine is produced in small quantities by the action of zinc dust. G. T. M.

**Nomenclature of the Diazo compounds.** By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2556—2559).—Since no sharp line of demarcation can be drawn between diazo- and azo-compounds from consideration either of stability or colour, it is proposed that all compounds of the general type  $R_1 \cdot N : N \cdot R_2$  be termed *azo*-compounds, irrespective of the nature of  $R_1$  and  $R_2$ ; the term diazo-compound is thus reserved only for fatty derivatives containing the group  $C \begin{smallmatrix} \diagup N \\ \diagdown N \end{smallmatrix}$ . To the soluble, dissociating

forms of diazo-compounds, the term "diazonium" is still to be applied; but the derivatives hitherto spoken of as *syn*- and *anti*-diazo-compounds will now be named *syn*- and *anti*-azo-compounds. A list of revised names for typical substances is appended. W. A. D.

**Decomposition of Diazonium Salts.** By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2517—2541).—[With GUSTAV OSSWALD.]—The rate of decomposition of a number of diazonium salts by water was compared by measuring in each case the rate of evolution of nitrogen. The velocity constant of benzenediazonium chloride at 25° is 0.00068; of *p*-toluenediazonium chloride, 0.000081; of *p*-bromediazonium chloride and anisediazonium chloride, too small for measurement; and of *ψ*-cumenediazonium chloride, 0.0031. The introduction of halogens into the benzene nucleus thus diminishes the tendency of diazonium salts to undergo decomposition with water; moreover, tribromobenzediazonium chloride is only decomposed on boiling with water, and then yields only resin and not tribromophenol. No relation exists, however, between the velocity constants of the formation of phenols and the affinity constants of the corresponding diazohydroxides; for although anisole and *ψ*-cumenediazonium hydroxides are equally strong bases, their rates of decomposition by water are entirely different.

[With W. SEMPLE.]—The decomposition of benzenediazonium chloride by 1 mol. of water yields 42 per cent. of phenol and 53 per cent. of chlorobenzene, whilst with 5 mols. of water only 46 per cent. of the latter is formed; with the corresponding diazonium bromide and 1 mol. of water, about 60 per cent. of bromobenzene is obtained. *ψ*-Cumenediazonium chloride, with 2 mols. of water, yields 52 per cent. of chloro-*ψ*-cumene, and the rest cumenol, whilst from the corresponding diazonium bromide 60 per cent. of bromo-*ψ*-cumene is obtained under similar conditions. With 1 mol. of glacial acetic acid, benzenediazonium chloride yields 57 per cent. of phenyl acetate and 43 per cent. of chlorobenzene, whilst with 10 mols., only 25 per cent. of chlorobenzene is produced; *ψ*-cumenediazonium bromide, with 2 mols. of acetic acid, yields 47 per cent. of cumenyl acetate and 53 per cent. of bromo-*ψ*-cumene, whilst with 40 mols., only 28 per cent. of the latter is obtained.

Benzenediazonium chloride, with cold absolute methyl alcohol, yields from 20 to 25 per cent. of anisole and a small amount of a hydrocarbon of high boiling point, probably diphenyl; on warming the same salt with ethyl alcohol, 25 per cent. of phenetole is obtained. With benzenediazonium bromide and methyl alcohol, the yield of anisole is only 10 per cent., but with ethyl alcohol, 30 per cent. of phenetole is obtained. *p*-Bromobenzenediazonium bromide yields, with ethyl alcohol, only a small quantity of *p*-bromoanisole, bromobenzene and resinous products being formed, whilst tribromobenzenediazonium bromide yields almost exclusively tribromobenzene and traces of tribromophenetole.

[With J. SPEAR.]—The decomposition of diazonium salts by hydriodic acid or potassium iodide in alcoholic or glacial acetic acid solution gives rise to large quantities of iodine, owing to the reduction by the hydriodic acid of the diazonium salt to the corresponding hydrocarbon.

In aqueous solution, the formation of iodine is diminished, but at the cost of production of phenol; increased dilution favours the liberation of iodine.

Benzenediazonium sulphate yields, with potassium iodide in *N*/20 solution at 10°, 40 per cent. of iodobenzene, the rest being transformed into phenol and resinous substances; *p*-toluenediazonium sulphate or chloride yields, in a similar solution at the ordinary temperature, 84 per cent. of *p*-iodotoluene, whilst *o*-toluenediazonium sulphate gave 53 per cent. of *o*-iodotoluene. *m*-Toluenediazonium sulphate, *as-m*-xylene-diazonium sulphate, and *ψ*-cumenediazonium sulphate, however, give rise only to the corresponding phenols without introduction of iodine into the nucleus, methyl groups thus impeding the latter action. Halogens, on the other hand, favour the introduction of iodine, for *p*-chlorobenzenediazonium sulphate, on boiling with *N*/20 aqueous potassium iodide, yields 72 per cent., *p*-bromobenzenediazonium sulphate 80 per cent., and tribromobenzenediazonium sulphate 94 per cent. of the iodo-derivative.

W. A. D.

### Interaction of Diazonium Salts with Cuprous Compounds.

By ARTHUR HANTZSCH and J. W. BLAGDEN (*Ber.*, 1900, **33**, 2544—2556).—Aqueous bromobenzenediazonium bromide interacts at 0° with cuprous chloride (1 mol.) suspended in water to form principally *p*-chlorobromobenzene, a small proportion only of *p*-dibromobenzene being obtained; *p*-bromobenzenediazonium chloride and cuprous bromide yield only *p*-dibromobenzene. When the copper haloid is dissolved in methyl sulphide and the diazonium salt added, either solid or dissolved in alcohol or glacial acetic acid, the action at 0° is similar, but more vigorous and complete. Cuprous iodide also yields, with diazonium chlorides or bromides, iodo-substituted benzenes; yet, mesitylene- and *ψ*-cumene-diazonium iodides with cuprous chloride yield as chief products the corresponding chloro- instead of the iodo-derivatives. The halogen introduced into the nucleus is thus derived principally from the cuprous salt, probably owing to the formation of an additive compound. In all these cases, a mixture of halogen derivatives is obtained.

*syn*-Diazocyanides are not changed by cuprous haloids even at the temperature of boiling methyl sulphide; yet, the *syn*-diazocyanides are rapidly converted into nitriles under the influence of copper powder, and diazonium haloids, by interaction with cuprous cyanide, form more nitrile than halogen-benzene. All attempts to prepare double salts of diazonium haloids with cuprous haloids failed, although double mercury salts of the type of *benzenediazonium nitrate mercuri-nitrite*,  $2C_6H_5 \cdot N_2 \cdot NO_3 \cdot Hg(NO_2)_2$ , are readily obtainable; the latter is precipitated on mixing concentrated solutions of potassium mercuri-nitrite and benzenediazonium nitrate, as an oil which rapidly crystallises. It is easily soluble in water, melts at 76°, and cannot be crystallised from water owing to its decomposing in the normal way to form phenol or nitrophenol; with copper powder, it yields nitrobenzene almost quantitatively. That the salt is not a double nitrite,  $2C_6H_5 \cdot N_2 \cdot NO_2 \cdot Hg(NO_2)_2$ , is shown by the fact that quite different substances are obtained on precipitating benzenediazonium sulphate

or chloride with potassium mercurinitrite, and that in these sulphuric acid and hydrochloric acid respectively are present. The double salts obtained with diazonium haloids are white, crystalline powders which are almost insoluble in water, and therefore do not decompose when stirred with copper powder; when boiled with water, they yield phenols.

On mixing solutions of potassium or sodium nitrite and cuprous chloride, a potassium cuprous nitrite is probably formed, since the mixture decomposes; for example, *p*-chlorobenzenediazonium sulphate forms *p*-nitrochlorobenzene along with *p*-dichlorobenzene. If, instead of the cuprous haloid, cuprous sulphite is employed, either in the form of the white Etard's salt, or, better, of the red cuprous cupri-sulphite (Chevreul's salt), a nearly theoretical yield of nitro-derivative is obtained on decomposing the diazonium salt; this method of replacing the amino-group by a nitro-group is shown to give much better results than Sandmeyer's process in the case of *p*-chloroaniline, *p*-bromoaniline, tribromoaniline, and especially  $\beta$ -naphthylamine. That it is the nitrite radicle combined with the copper that replaces the diazonium group in these cases, as in the preceding, is shown by the fact that *p*-chlorobenzenediazonium chloride yields a mixture of 74 per cent. of *p*-chloronitrobenzene and only 26 per cent. of *p*-dichlorobenzene.

Attempts to introduce a nitroso-group in place of the diazonium radicle by means of "cuprous hyponitrite," and a fluorine atom by means of "cuprous fluoride," failed.

$\psi$ -Cumenediazonium salts with cuprous haloids give rise to azo- $\psi$ -cumene, the yield amounting to 50—70 per cent. of the theoretical.

W. A. D.

**New Method of Preparing *iso*Diazotates.** By EUGEN BAMBERGER and JENS MÜLLER (*Annalen*, 1900, 313, 97—128).—The authors have found that *o*- or *p*-hydroxybenzylated arylnitroso-derivatives of the type  $\text{NO} \cdot \text{N} \cdot \text{Ar} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , are resolved by very dilute potassium hydroxide into hydroxybenzyl alcohol and potassium *isodiazotate*,  $\text{ArN} \cdot \text{N} \cdot \text{OK}$ ; the change does not occur when the hydroxy-group occupies the meta-position, or when other radicles replace hydroxyl.

*Phenyl o-hydroxybenzylnitrosoamine*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$ , crystallises from dilute methyl alcohol in pale yellow prisms melting at  $131.5^\circ$ . The hydrolysis was effected under very various conditions, which are fully described in the paper. Alkali was employed alone, or in presence of certain phenols, also at the temperatures of melting ice and boiling water; in each case, the *isodiazotate* was produced, and not the normal compound.

*Phenyl-p-hydroxybenzylnitrosoamine* crystallises from alcohol in flat, straw-yellow prisms and melts at  $120^\circ$ .

*m-Hydroxybenzylideneaniline*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{NPh}$ , prepared from aniline and *m*-hydroxybenzaldehyde, crystallises from benzene in lustrous, colourless aggregates of prisms, and melts at  $90.5-91^\circ$ .

*m-Hydroxybenzylaniline*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh}$ , obtained on reducing the Schiff base with sodium amalgam in alcohol, crystallises from dilute alcohol in short prisms and melts at  $103-104^\circ$ ; the *nitroso*-

derivative,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$ , separates from dilute alcohol in lustrous, colourless needles melting at  $87.5-88^\circ$ , and is practically indifferent towards alkali hydroxides.

*o*-Hydroxybenzyl-*p*-tolylnitrosoamine,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{NO}$ , crystallises from dilute acetic acid in feathery aggregates of colourless needles and melts at  $74.5-75^\circ$ ; its behaviour towards alkali hydroxides resembles that of its lower homologue.

*o*-Chlorobenzylideneaniline,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH} \cdot \text{NPh}$ , prepared from aniline and *o*-chlorobenzaldehyde, is a yellow, viscous oil. *o*-Chlorobenzylaniline,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{NHPh}$ , obtained on reducing the Schiff base, is also a viscous oil, forming the crystalline *hydrochloride* which melts, not quite definitely, at  $186-187^\circ$ ; the *nitroso*-derivative,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$ , separates from alcohol in pale yellow, lustrous leaflets melting at  $53.5-54^\circ$ , and is indifferent towards alkali hydroxides.

Other substances, which do not yield *isodiazotates* under the influence of alkali hydroxides, are *o*-nitrobenzylphenylnitrosoamine, which has been prepared by Busch, and *p*-nitrobenzylphenylnitrosoamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$ , which crystallises in pale yellow, transparent leaflets and melts at  $75.5-76^\circ$ .

*Phenyl-as-o-hydroxybenzylhydrazine*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NH}_2$ , prepared by reducing the nitrosoamine of *o*-hydroxybenzylaniline with zinc dust in acetic acid solution, is conveniently isolated in the form of the *m-nitrobenzylidene* derivative,  $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_3$ , which crystallises from alcohol in radially disposed, orange red needles melting at  $183-183.5^\circ$ .

M. O. F.

*syn*-Diazotates from *p*-Bromodiazobenzene-*o*-sulphonic Acid. By DIMITER W. GERILOWSKI (*Ber.*, 1900, 33, 2317-2323).—*p*-Bromo-

*benzenediazonium-o-sulphonic acid*,  $\text{C}_6\text{H}_3\text{Br} \begin{smallmatrix} \text{SO}_2 \\ \diagup \quad \diagdown \\ \text{N}(\text{:N}) \end{smallmatrix} \text{O}$ , obtained by the diazotisation of *p*-bromoaniline-*o*-sulphonic acid, crystallises in silky, colourless, six-sided plates, decomposes at  $149^\circ$ , forms a neutral aqueous solution and does not detonate when struck. The *syn-disodium salt*,  $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_3\text{Br} \begin{smallmatrix} \text{N} \\ | \\ \text{ONa} \cdot \text{N} \end{smallmatrix}$ , obtained by treating the acid

with sodium hydroxide below  $0^\circ$ , crystallises, with  $\text{H}_2\text{O}$ , in yellow crystals, forms an alkaline solution in water, couples instantly with  $\beta$ -naphthol and is quite stable when kept in a desiccator. The *anti-disodium salt* is obtained when the mother liquors left from the crystallisation of the *syn*-salt are heated; it crystallises in small clusters, and does not couple with an alkaline solution of  $\beta$ -naphthol until it has been converted into the isomeric form by acidifying and subsequent neutralisation. The corresponding *syn-dipotassium salt* crystallises, with  $4\text{H}_2\text{O}$ , in sharp-pointed plates, becomes reddish in colour when exposed to air, and, when heated to  $100^\circ$ , is converted into the *anti dipotassium salt*, which crystallises, with  $\text{H}_2\text{O}$ , in dark, greenish-yellow, striated prisms.

R. H. P.

Diazohydrazides and Bisdiazotetrazones (Octazones). By ALFRED WOHL and HANS SCHIFF (*Ber.*, 1900, 33, 2741-2758).—By the action of diazobenzene sulphate on hippurylhydrazine, Curtius (*Abstr.*, 1893, i, 463) obtained a compound to which he gave the name



*sym*-hippurylphenylbuzylene, being derived from the hypothetical compound  $\text{NH}\cdot\text{N}\cdot\text{NH}\cdot\text{NH}_2$ . The authors have prepared a number of similar substances and suggest that it would be simpler to name them 'diazohydrazides,' which allows isomerides to be readily distinguished and is in better agreement with the chemical characters of the compounds. A study of the possible methods of condensation of a diazo-compound with a hydrazine with evolution of water, together with the fact that two isomeric compounds  $\text{R}^{\text{I}}(\text{N}_4\text{H}_2)\text{R}^{\text{II}}$  and  $\text{R}^{\text{II}}(\text{N}_4\text{H}_2)\text{R}^{\text{I}}$  exist which yield different oxidation products, shows that the diazohydrazides have the constitution  $\text{NR}^{\text{I}}\cdot\text{N}\cdot\text{NR}^{\text{II}}\cdot\text{NH}_2$ . Formation of these compounds takes place only at low temperatures and in presence of free acetic acid. They are mostly well crystallisable substances of a yellow or brown colour and more or less soluble in alcohol, ether, acetone, or benzene, less so in light petroleum, and, except in the case of derivatives of strongly basic hydrazines, insoluble in water or dilute acids. When heated on a spatula or with a hot glass rod, they explode but not when rubbed or struck. Those soluble in alkalis, such as diazobenzoic acid phenylhydrazide, reduce Fehling's solution. The yields obtained are small (in general 20—40 per cent.), as the reaction between the diazo-compound and the hydrazine goes partly in those directions which it takes in presence of mineral acids. On oxidation with permanganate, the diazohydrazides yield bisdiazotetrazones or octazones, which have the constitution  $\text{NR}^{\text{I}}\cdot\text{N}\cdot\text{NR}^{\text{II}}\cdot\text{N}\cdot\text{N}\cdot\text{NR}^{\text{II}}\cdot\text{N}\cdot\text{NR}^{\text{I}}$  and contain the longest chain of nitrogen atoms known. They are generally light in colour but quickly darken under the action of light and air and explode when subjected to heat, friction, or impact; they dissolve in the organic solvents with the exception of light petroleum, but quickly decompose in solution.

*Bisdiazobenzenediphenyltetrazone*,  $\text{N}_2(\text{NPh}\cdot\text{N}_2\text{Ph})_2$ , obtained in small quantity on oxidising diazobenzenephenylhydrazide, melts at 51—52°.

*p*-Chlorodiazobenzenephenylhydrazide,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\cdot\text{NPh}\cdot\text{NH}_2$ , melts at 78°; *p*-bromodiazobenzenephenylhydrazide, melts at 79°, and on oxidation with permanganate yields *bis-p*-bromodiazobenzenediphenyltetrazone,  $\text{N}_2(\text{NPh}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br})_2$ , melting at 60°.

*Diazobenzene-p*-bromophenylhydrazide,  $\text{NPh}\cdot\text{N}\cdot\text{N}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\text{Br}$ , melts at 69° and explodes 10° lower than its isomeride described above.

*p*-Bromodiazobenzenep-bromophenylhydrazide,  
 $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\cdot\text{N}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\text{Br}$ ,  
 melts at 82—84° and its oxidation product, *bis-p*-bromodiazobenzenedi-1:4-bromophenyltetrazone,  $\text{N}_2[\text{N}(\text{C}_6\text{H}_4\text{Br})\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br}]_2$ , at 58—61°.

*p*-Diazotoluenephenylhydrazide,  $(\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{NPh}\cdot\text{NH}_2)$ , melts at 66—67°, and on boiling with dilute sulphuric acid, decomposes with brisk evolution of nitrogen and the formation of almost the theoretical quantity of *p*-cresol, together with phenylhydrazine sulphate, and a little diazotolueneimine. *Bis-p*-diazotoluenediphenyltetrazone,

$\text{N}_2(\text{NPh}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$ ,  
 melts at 64—67°, and dissolves slowly in ether with evolution of gas and formation of diazobenzenetoluidide.

*Diazobenzene-p*-tolylhydrazide,  $\text{NPh}\cdot\text{N}\cdot\text{N}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\text{Me}$ , is a relatively stable compound melting at 64—65°, and on boiling with dilute

sulphuric acid yields phenol and *p*-tolylhydrazine sulphate. *Bisdiazobenzene-p-tolyltetrazone*,  $N_2[N(C_6H_4Me) \cdot N_2Ph]_2$ , melts at  $55^\circ$ .

*m-Diazobenzoic acid phenylhydrazide*,  $CO_2H \cdot C_6H_4 \cdot N_2 \cdot NPh \cdot NH_2$ , is an amorphous, yellow substance melting at  $108-112^\circ$ , and is soluble in aqueous sodium carbonate, giving a solution which reduces Fehling's solution; on boiling its benzene solution, it decomposes into the imine of diazobenzoic acid and aminobenzoic acid.

*p-Diazobenzoic acid phenylhydrazide* melts at  $112-113^\circ$ .

*Diazobenzene-m-hydrazinobenzoic acid*,  $N_2Ph \cdot N(NH_2) \cdot C_6H_4 \cdot CO_2H$ , melts at  $86^\circ$ , and on boiling with dilute sulphuric acid yields phenol and hydrazinobenzoic acid.

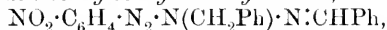
*p-Nitrodiazobenzenemethylhydrazide*,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NMe \cdot NH_2$ , crystallises from benzene or aqueous alcohol in brown needles having a bronzy lustre and melting at  $120-122^\circ$ . By the action of benzaldehyde, it yields *p-nitrodiazobenzenebenzylidenemethylhydrazide*,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NMe \cdot N:CHPh$ ; this separates from light petroleum in slender, yellowish-red needles which melt and evolve gas at  $148^\circ$  and explode at higher temperatures; it is readily soluble in acetone, less so in benzene, alcohol, ether, or acetic acid, and is precipitated unchanged from the last-named solvent by sodium carbonate.

*Diazobenzenebenzylhydrazide*,  $N_2Ph \cdot N(NH_2) \cdot CH_2Ph$ , crystallises from light petroleum in white, hexagonal leaflets which melt and evolve gas at  $46-48^\circ$ .

*p-Nitrodiazobenzenebenzylhydrazide*,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot N(NH_2) \cdot CH_2Ph$ , separates from alcohol in dark brown, shining, flat prisms melting at  $94-96^\circ$ , and exploding at a higher temperature; it dissolves readily in benzene or acetone, less so in alcohol or ether, and only slightly in acetic acid or light petroleum. Oxidation with permanganate does not yield the corresponding tetrazone derivative, but its decomposition products.

*p-Nitrodiazobenzenebenzylamine*,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot CH_2Ph$ , melts at  $99^\circ$ .

*p-Nitrodiazobenzenebenzylbenzylidenehydrazide*,



prepared either from *p*-nitrodiazobenzenebenzylhydrazide and benzaldehyde, or from nitrodiazobenzene and benzylbenzylidenehydrazone, crystallises from alcohol in pale yellow needles melting at  $142-143^\circ$ , and is soluble in benzene, acetone, light petroleum, ether, or acetic acid; it is a stable substance, and is only decomposed by long boiling with dilute acids.

T. H. P.

**First Cleavage Product of Proteid by the Action of Alkali.** By OTTO MAAS (*Zeit. physiol. Chem.*, 1900, 30, 61-74).—After the action of solution of the alkalis on egg-albumin and crystallised serum albumin, the following substances were sought for: (1) Proto- and hetero-albumose, by the addition of an equal volume of saturated ammonium sulphate; (2) A-albumose, by the addition of another volume of ammonium sulphate solution to the filtrate from (1); (3) B-albumose, by the saturation of the filtrate from (2) by ammonium sulphate; (4) C-albumose, by the addition of *N*/10 sulphuric acid to

the filtrate from (3); (5) peptone, by the occurrence of the biuret reaction in the final filtrate. A-, B-, and C-albumoses and peptone were absent, or present in the merest traces. The primary albumoses were not abundant, but the main product, called alkali-albumose, was precipitated by neutralisation; it resembles Gmelin's albuminic acid very closely. Its composition is, C, 53.57; H, 7.19; N, 13.62; S, 2.13; O, 23.49 per cent. Its rotatory power is  $[\alpha]_D - 49.4$ .

W. D. H.

**Albumin in Ox-Serum.** By HOUARDY (*Chem. Centr.*, 1900, ii, 682; from *Bull. Acad. roy. Belg.*, 1900, 401—413).—According to Halliburton the blood serum of hooved animals contains two albumins coagulating at 77° and 82—84° respectively. The author's attempts to separate these albumins by fractional precipitation with ammonium sulphate have shown, however, that only one albumin is present although its temperature of coagulation is not constant. The following experiments on coagulation are also described. (1) Albumins which coagulated at 72° and 80° respectively, were found to be completely coagulated after heating for 5—6 hours at 65°. (2) The filtrate from a portion of the liquid, after heating for 3 or 4 hours at 65°, contained a small quantity of albumin which coagulated at 80—81°. (3) A neutral solution of albumin containing exactly 3 per cent. of ammonium sulphate was coagulated by heating to 72°. After filtering, the whole of the albumin was precipitated by ammonium sulphate and then dissolved in water so that the solution again contained 3 per cent. of ammonium sulphate. This solution was found to coagulate at 72° and on repeating the process, the third solution coagulated at 71° and the filtrate was free from albumin.

E. W. W.

**Action of Dilute Acids, Alcohol, and Heat on Columbiniin.** By ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 385—390. Compare *ibid.*, 1897, 29, 398; this vol., i, 126).—With hydrogen chloride, columbiniin forms the compound  $\text{Cb}_5\text{HCl}$  and with hydrogen bromide,  $\text{Cb}_4\text{HBr}$ , where Cb represents  $\text{C}_{251}\text{H}_{415}\text{O}_{96}\text{N}_{56}\text{S}_2$ . When the hydrochloride is heated with 0.1 per cent. hydrochloric acid, its specific rotation is increased but its composition remains unchanged. If precipitated from aqueous solutions by warming or by the addition of alcohol, columbiniin is obtained in an insoluble form, whilst if the solution is evaporated in a vacuum, the columbiniin obtained is soluble; the products obtained in this way are regarded as polymerides of columbiniin.

T. H. P.

**Colouring Matter of Blood.** By MARCELLUS NENCKI AND J. ZALESKI (*Zeit. physiol. Chem.*, 1900, 30, 381—435. Compare Abstr., 1885, 69, 70, 566, 825, 826; 1896, i, 516, 660; 1897, i, 207, 232; 1898, i, 542; 1899, ii, 440). I. *Hæmin Ethers*.—When hæmoglobin is extracted with an acetic acid solution of sodium chloride by the Teichmann-Schälféeff method (Abstr., 1885, 69) the product is *acetyl-hæmin*,  $\text{C}_{31}\text{H}_{33}\text{O}_4\text{N}_4\text{ClFe}$ ; the same product is obtained from the blood of the dog, horse, cow, cat, and goose. It crystallises in microscopic

triclinic plates and prisms, readily dissolves in dilute alkalis, ammonia, or solutions of organic bases, but is insoluble in dilute mineral or organic acids. It probably contains both chlorine and acetyl attached to the iron atom, as when the latter is removed by the action of hydrobromic acid, both chlorine and the acetyl group are withdrawn from the molecule. Cold sodium hydroxide removes chlorine and acetyl group but not iron; the hydrolysis is not complete as the hæmatin thus obtained always contains minute quantities of chlorine. The hæmin obtained by Nencki and Sieber's method yields the same hæmatin on hydrolysis. Acetyl hæmin contains no alkyl groups attached to oxygen or nitrogen, but two hydroxyl groups are present, as it readily yields mono- and di-ethers. The substances obtained by different authorities by the action of alcohols and hydrochloric acid on hæmoglobin are probably ethers of hæmin or of acetyl hæmin.

*Hæmin dimethyl ether*,  $C_{32}H_{29}(OMe)_2ON_4ClFe$ , obtained when acetyl hæmin is dissolved in a chloroform solution of quinine and then treated with methyl alcohol saturated with hydrogen chloride, forms whetstone shaped crystals, is completely insoluble in alkalis, and does not melt at  $300^\circ$ . *Acetyl hæmin ethyl ether* is identical with the compound described by Möerner as  $\beta$ -hæmin; when boiled with potassium hydroxide it evolves ethyl alcohol, and dissolves readily as it contains a free hydroxyl group. *Acetyl hæmin diethyl ether* forms black, cubical crystals and is insoluble in alkalis. Cloetta's hæmin hydrochloride is essentially a mixture of the di- and mono-ethyl ethers. The *amyl ether*,  $C_{34}H_{32}(C_5H_{11})O_4N_4ClFe$ , forms spindle-shaped crystals readily soluble in chloroform, but only sparingly so in aqueous ammonia, it does not melt at  $350^\circ$ . In the preparation of these ethers, the formation of large hexagonal plates has been observed, but their composition has not been determined.

When hæmoglobin is extracted with acetone, the product is not homogeneous, but contains dark coloured hair-like needles, which appear to be hæmin,  $C_{32}H_{31}O_3N_4FeCl$ , as on treatment with acetic acid they yield the acetyl hæmin already described. When ethyl acetate and hydrochloric acid are employed as extractive agents, the product consists of acetyl hæmin and its ethyl ether.

The authors do not consider Preyer's synthesis of hæmoglobin (Abstr., 1897, i, 304) as established.

II. *Hæmatoporphyrin*.—In the preparation of hæmatoporphyrin (Abstr., 1888, 971), it is advisable to use small quantities of hæmin, and to leave it in contact with concentrated hydrobromic acid for three days at the ordinary temperature. Hæmin, acetyl hæmin, and its ethers all yield the same hæmatoporphyrin,  $C_{16}H_{18}O_3N_2$  (compare Bialobrzewski, Abstr., 1897, i, 208, and Küster, *ibid.*, 232). It yields an unstable ammonium salt and a *dimethyl ether*,  $C_{16}H_{16}(OMe)_2ON_2$ , which forms an amorphous, brick-red powder, and readily turns brown; it begins to sinter at  $60^\circ$ , and is completely melted at  $85^\circ$ . The *diethyl ether* also melts below  $100^\circ$ , evolving ethyl alcohol; it is insoluble in dilute acids or alkalis, and only sparingly soluble in ether or benzene. An *anhydro-monoacetyl hæmatoporphyrin*,  $C_{32}H_{31}AcO_4N_4$ , obtained by the action of acetic anhydride and sodium acetate, forms an amorphous, brown-red powder.

All attempts to remove the oxygen atoms from hæmatoporphyrin proved unsuccessful. J. J. S.

**Crystals from Pigeons' Blood.** By ARTHUR SCHWANTKE (*Zeit. physiol. Chem.*, 1900, 29, 486—491).—Sphenoidally-hemihedral tetragonal crystals [ $a:c=1:1.175$ ] of oxyhæmoglobin obtained from pigeons' blood are described, with drawings of the different habits assumed; the crystals are characterised by a tendency to parallel growth, and can be kept several months at a low temperature without the brightness or relative distribution of the faces being impaired, although internally the crystals lose their transparency and become isotropic. W. A. D.

**Hæmatin and Hæmochromogen obtained by the use of Pepsin-hydrochloric Acid.** By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1900, 30, 126—134).—Hæmatin obtained by different methods has been analysed, and different results obtained. The method recommended here is to digest a solution of hæmoglobin crystals with pepsin-hydrochloric acid. Tryptic digestion leads to no result. At the end of some days, the bulk of the hæmatin so formed is precipitated as a brown powder; this is suitably washed and collected, and from it hæmin crystals are prepared by the addition of acetone and hydrochloric acid. The crystals are dichroic, and belong either to the monoclinic or trichlinic system. Analytical results correspond with those required for the formula  $C_{34}H_{34}O_4N_5ClFe$ , containing one atom of nitrogen more than in Hoppe-Seyler's and Mörner's preparations. If dissolved in dilute alkali, a precipitate of hæmatin of the formula  $C_{34}H_{35}O_5N_5Fe$  is obtained on adding dilute sulphuric acid. From this, hæmochromogen can be prepared. It is doubtful from the analyses whether the formula for this substance is  $C_{34}H_{38}O_4N_6Fe$  or  $C_{68}H_{76}O_9N_{12}Fe_2$ . By electrolysis of hæmatin solutions, hæmochromogen was not obtained. If pyridine is added to a solution of hæmatin and then hydrazine hydrate, hæmochromogen is produced. W. D. H.

**Aldehydase from the Liver and Suprarenal Capsule.** By MARTIN JACOBY (*Zeit. physiol. Chem.*, 1900, 30, 135—148. Compare Abstr., 1899, ii, 778).—The oxidising ferments in the liver are probably numerous; the one investigated in the present research is termed *aldehydase* and oxidises salicylaldehyde. A similar ferment can be separated from the cortex of the suprarenal capsule. Evidence is adduced that the action is fermentative. It was separated from aqueous extracts of the liver by precipitation with ammonium sulphate, the ferment coming down with the final fractions; the precipitate was dissolved in water, again precipitated with alcohol, and again dissolved in water; this solution was made faintly alkaline to prevent precipitation of proteids, and precipitated with uranium acetate; the final precipitate was dissolved in water. The enzyme is a colloid (non-dialysable); under a pressure of 6 atmospheres, however, it passes through a porcelain cell. It is not proteid, and does not give the biuret or Millon's reaction. W. D. H.

**Proteolytic Enzyme of Germinated Barley.** By WILHELM WINDISCH and B. SCHELLHORN (*Chem. Centr.*, 1900, ii, 489—490, 490—491; from *Woch. Brav.*, 17, 334—336, 437—439, 449—452).—From their lengthy researches on the proteolytic enzyme contained in malt, the authors draw the following conclusions: (1) Under conditions favourable to the action of animal enzymes, the enzyme does not attack albumin which has been rendered insoluble; (2) the enzyme only gives the biuret reaction when it is in contact with albumins or albuminous substances of animal origin; (3) the decomposing action of the enzyme can only be recognised by its action on albumins which are in a soluble form. E. W. W.

**Galactase, the Proteolytic Ferment peculiar to Milk, its Properties, and Action on the Proteids of Milk.** By S. MOULTON BABCOCK and H. L. RUSSELL (*Centr. Bakt. Par.*, 1900, [ii], 6, 17—21, 45—50, and 79—88).—Galactase (previously described by the authors, *Centr. Bakt. Par.*, [ii], 3, 615) is a proteolytic ferment similar to trypsin and is present in the milk of all animals. It is more active in moderately alkaline than in neutral or faintly acid solutions. Comparative experiments are described, in which the action of all proteolytic ferments of animal origin on milk is tabulated.

Pepsin differs from all other proteolytic ferments in that it causes no alteration in the amount of soluble nitrogen compounds in milk which has been treated with other ferments. A large proportion of the nitrogen present in milk is not attacked by these ferments; the greater part of this is the nuclein of the proteid molecules, but some is due to the accumulation of decomposition bye products, which hinder the digestion. The proteids are attacked by all the ferments with the formation of albumoses, amino-compounds, and sometimes even ammonia. Trypsin and pancreatin differ from galactase and from the proteolytic ferment derived from a culture of *Bacillus subtilis* in not forming ammonia; galactase differs from the latter in that the nitrogen compounds formed in digestion by its agency are more equally divided in albumoses, peptones, amides, and ammonia. R. H. P.

**The Organised Ferment present in Milk, the so called Galactase.** By ED. VON FREUDENREICH (*Centr. Bakt. Par.*, 1900, [ii], 6, 332—338. Compare *ibid.*, 3, 615).—The author has repeated and confirms the researches of Babcock and Russell (*loc. cit.* and preceding abstract). Formalin or a temperature of 75° weakens the action of the galactase. R. H. P.

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